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Practical synthesis of enantiopure benzylamines by catalytic hydrogenation or transfer hydrogenation reactions in isopropanol using a Ru-pybox catalyst

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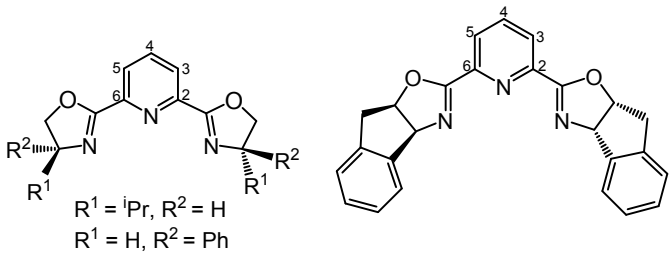
SUPPORTING INFORMATION

General Experimental Procedures. Manipulations with air sensitive compounds were performed under an atmosphere of dry nitrogen or argon either using standard Schlenk techniques or a glove-box. The reagents were obtained from commercial suppliers and used without further purification. Solvents were dry by standards methods and distilled under nitrogen or argon before use. Imines **4** were prepared as described previously.[S1] Complexes *trans*-[RuCl(μ-Cl)(η^6-$C_{10}H_{14}$)]$_2$,[S2] *trans*-[RuCl$_2$(η^2-C_2H_4){(*R*,*R*)-Ph-pybox}],[S3] *trans*-[RuCl$_2$(η^2-C_2H_4){(*S*,*S*)-^{i}Pr-pybox}],[S3, S4] and *trans*-[RuCl$_2$(η^2-C_2H_4){(3a*S*,3a´*S*,8a*R*,8a´*R*)-indane-pybox}],[S5] as well as ligands (*R*,*R*)-Ph-pybox,[S6] (*S*,*S*)-^{i}Pr-pybox[S7] and 3a*S*,3a´*S*,8a*R*,8a´*R*)-indane-pybox[S8] were synthesized by reported methods. Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. The C,H, N analyses were carried out with a LECO CHNS-TruSpec and a Perkin-Elmer 240-B microanalyzers. Electrospray mass spectra (ESI-MS) were recorded on a Bruker Esquire 6000 spectrometer, operating in the positive mode and using dichloromethane/methanol solutions. NMR spectra were recorded on Bruker DPX-300, DRX-400, AV-400 or DRX-500 spectrometers. The values of chemical shifts are given in parts per million (ppm) and referenced to TMS or 85 % H_3PO_4 as standards. The values for coupling constants (*J*) are given in Hz. Assignment of some ^{1}H NMR spectra was aided by the use of 2D ^{1}H-^{13}C HSQC experiments. HPLC analyses were performed by using a Waters 2690 chromatograph, these analyses were performed at 303 K.

The following atoms labels have been used for the ^{1}H and ^{13}C{^{1}H} spectroscopic data of the pybox ligands.



Synthesis of complexes *trans*-[RuCl$_2$(CNR){(*R*,*R*)-Ph-pybox}] (R = Bn (1k), Cy(1l)). To a solution of the complex *trans*-[RuCl$_2$(η^2-C$_2$H$_4$){(*R*,*R*)-Ph-pybox}] (0.030 g, 0.05 mmol) in dichloromethane (10 mL) was added an excess of isocyanide (0.15 mmol) and the mixture heated at 55º C in a sealed tube for 3.5 h (**1k**) or 5 h (**1l**). Then, the solvent was evaporated under reduced pressure and *n*-hexane (20 mL) was added affording a solid residue. The solvent was decanted and the resulting solid washed with *n*-hexane (3 x 5 mL) and vacuum-dried.

*Complex **1k***: Color: dark pink. Yield 81 % (0.027 g). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 7.93 (m, 3H, H^{3,4,5} C_5H_3N), 7.44–7.25 (m, 13H, Ph), 7.03 (m, 2H, Ph), 5.28 (m, 4H, OCH_2, C*H*Ph), 4.58 (m, 2H, OCH_2), 4.37 (m, 2H, CH_2Ph) ppm. ^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K): δ = 166.0 (s, OCN), 148.7 (s, C^{2,6} C_5H_3N), 137.8 (s, *C*NCH$_2$), 137.6 (s, C^{ipso} Ph), 135.2 (s, C^4 C_5H_3N), 134.2 (s, C^{ipso} Ph), 128.7, 128.4, 128.1, 128.0, 127.4, 126.3 (6*s*, Ph), 122.7 (s, C^{3,5} Ph), 78.5 (s, OCH_2), 70.3 (s, *C*HPh), 47.1 (s, *C*H$_2$Ph) ppm. IR (KBr, cm^{-1}): ν(C≡N) 2128 (vs). ESI-MS: *m/z* = 682.2 [RuCl$_2$(CNBn)(Ph-pybox) + Na]$^+$, 623.3 [RuCl(CNBn)(Ph-pybox)]$^+$, 506.2 [RuCl(Ph-pybox)]$^+$. Elemental analysis calcd (%) for $C_{31}H_{26}Cl_2N_4O_2Ru{\cdot}CH_2Cl_2$ (742.98): C 51.70, H 3.80, N, 7.54; found: C, 51.26, H 3.58, N, 7.43.

*Complex **1l***: Color: Purple. Yield 80 % (0.026 g). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 7.93 (m, 3H, H^{3,4,5} C_5H_3N), 7.48 (d, *J*(H,H) = 7.2 Hz, 4H, Ph), 7.35 (m, 6H, Ph), 5.26 (m, 4H, OCH_2, C*H*Ph), 4.52 (m, 2H, OCH_2), 3.38 (m, 1H, NCH), 1.89 (m, 2H,

CH_2 Cy), 1.45 (m, 2H, CH_2 Cy), 1.31 (m, 2H, CH_2 Cy), 1.10 (m, 2H, CH_2 Cy), 1.01 (m, 2H, CH_2 Cy) ppm. ^{13}C {^1H} NMR (101 MHz, CD_2Cl_2, 298 K): δ = 166.3 (s, OCN), 148.5 (s, $C^{2,6}$ C_5H_3N), 138.2 (s, C^{ipso} Ph), 134.5 (s, C^4 C_5H_3N), 128.4, 128.3, 127.9 (3*s*, Ph), 122.6 (s, $C^{3,5}$ C_5H_3N), 78.5 (s, OCH_2), 70.2 (s, *C*HPh), 53.6 (s, NCH), 32.6, 25.1, 24.9, 22.6, 22.5 (5*s* CH_2 Cy) ppm. IR (KBr, cm^{-1}): ν(C≡N) 2126 (vs). ESI-MS: *m/z* = 673.2 $[RuCl_2(CNCy)(Ph\text{-}pybox) + Na]^+$, 615.4 $[RuCl(CNCy)(Ph\text{-}pybox)]^+$, 506.2 $[RuCl(Ph\text{-}pybox)]^+$. Elemental analysis calcd (%) for $C_{30}H_{30}Cl_2N_4O_2Ru \cdot 0.5\ CH_2Cl_2$ (693.03): C 52.86, H 4.51, N 8.08; found: C 53.30, H 4.44, N 7.85.

Synthesis of complexes *trans*-[$RuCl_2$(L){(*R*,*R*)-Ph-pybox}] (L = $PPh_2(OMe)$ (1h), $PPh_2(OEt)$ (1i), $PPh(OMe)_2$ (1j)). To a solution of complex *trans*-[$RuCl_2$(η^2-C_2H_4){(*R*,*R*)-Ph-pybox}] (**1a**) (0.1 g, 0.176 mmol) in toluene (30 mL) the corresponding phosphonite or phosphinite (0.2 mmol) was added and the mixture heated at 130 ºC in a sealed tube during 1h 45 min The solvent was then evaporated under reduced pressure and the solid residue was purified by chromatography over silica gel. Elution with a mixture of dichloromethane/methanol (50:1) gave a purple band from which the corresponding complexes **1h-1j** were isolated by solvent removal.

*Complex **1h***. Color: Purple. Yield 84 % (0.112 g). ^1H NMR (300.13 MHz, CD_2Cl_2, 298 K): δ = 8.00 (m, 4H, $H^{3,5}$ C_5H_3N, Ph), 7.88 (m, 1H, H^4 C_5H_3N), 7.41-7.20 (m, 12H, Ph), 6.86 (m, 4H, Ph), 6.62 (m, 2H, Ph), 5.06 (m, 2H, OCH_2), 5.01 (m, 2H, C*H*Ph), 4.51 (m, 2H, OCH_2), 2.49 (d, ^3J(H,P) = 9.3 Hz, 3H, POMe) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K): δ = 166.6 (s, OCN), 148.1 (s, $C^{2,6}$ C_5H_3N), 139.4 (s, C^{ipso} Ph), 136.8 (d, J(C,P)= 29.4 Hz, C^{ipso} PPh), 135.5 (d, J(C,P) = 42.4 Hz, C^{ipso} PPh), 135.2 (s, C^4 C_5H_3N), 134.0 (d, ^2J(C,P) = 11.1 Hz, PPh), 131.7 (d, ^2J(C,P) = 10.3 Hz, PPh), 130.2, 128.3, 128.1 (3*s*, Ph), 127.6-127.5 (Ph), 126.6 (d, ^3J(C,P) = 8.6 Hz, PPh), 123.0 (s, $C^{3,5}$ C_5H_3N), 79.5 (s, OCH_2), 70.0 (s, *C*HPh), 52.8 (d, ^2J(C,P) = 14.1 Hz, POMe) ppm.

$^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2, 298 K): δ = 143.2 ppm. MS-ESI (*m/z*) = 779.9 $[RuCl_2(Ph\text{-}pybox)\{PPh_2(OMe)\}+Na]^+$ (24%), 757.0 $[RuCl_2(Ph\text{-}pybox)\{PPh_2(OMe)\}]^+$ (15%), 722.0 $[RuCl(Ph\text{-}pybox)\{PPh_2(OMe)\}]^+$ (100%). Elemental analysis calcd (%) for $C_{36}H_{32}Cl_2N_3O_3PRu$ (757.61 g/mol): C 57.07, H 4.26, N 5.55; found: C 57.23, H 4.74, N 5.11.

*Complex **1i***. Color: Purple. Yield 88 % (0.119 g). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 8.05-7.93 (m 5H, $H^{3,4,5}$ C_5H_3N, Ph), 7.45 (m, 2H, Ph), 7.35 (m, 2H, Ph), 7.29-7.16 (m, 8H, Ph), 6.84 (m, 4H, Ph), 6.64 (m, 2H, Ph), 5.04 (m, 4H, C*H*Ph, OCH_2), 4.52 (m, 2H, OCH_2), 3.19 (m, 1H, $POCH_2$), 2.83 (m, 1H, $POCH_2$), 0.24 (pt, *J*(H,H) = 6.8 Hz, 3H, CH_3) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2, 298 K): δ = 166.7 (s, OCN), 148.1 (s, $C^{2,6}$ C_5H_3N), 139.6 (s, C^{ipso} Ph), 137.5 (d, *J*(C,P) = 27.7 Hz, C^{ipso} PPh), 136.3 (d, *J*(C,P) = 38.6 Hz, C^{ipso} PPh), 135.1 (s, C^4 C_5H_3N), 133.9 (d, ^{2}J(C,P) = 10.9 Hz, PPh), 131.8 (d, ^{2}J(C,P) = 9.9 Hz, PPh), 130.0 (s, Ph), 128.2-127.4 (Ph), 126.6 (d, ^{3}J(C,P) = 8.2 Hz, PPh), 123.0 (s, $C^{3,5}$ C_5H_3N), 79.8 (s, OCH_2), 69.8 (s, C*H*Ph), 62.3 (d, ^{2}J(C,P) = 11.8 Hz, $POCH_2$), 15.5 (s, CH_3) ppm. $^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2, 298 K): δ = 141.3 ppm. MS-ESI (*m/z*) = 794.0 $[RuCl_2(Ph\text{-}pybox)\{PPh_2(OEt)\}+Na]^+$ (22%), 771.1 $[RuCl_2(Ph\text{-}pybox)\{PPh_2(OEt)\}]^+$ (37%), 736.0 $[RuCl(Ph\text{-}pybox)\{PPh_2(OEt)\}]^+$ (100%). Elemental analysis calcd (%) for $C_{37}H_{34}Cl_2N_3O_3PRu$ (771.64 g/mol): C 57.59, H 4.44, N 5.45; found: C 57.36, H 4.59, N 5.06.

*Complex **1j***. Color: Purple. Yield 70 % (0.088 g). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 8.05 (m, 1H, H^4 C_5H_3N), 7.96 (m, 2H, $H^{3,5}$ C_5H_3N), 7.37 (m, 6H, Ph), 7.24 (m, 5H, Ph), 7.12 (t, *J*(H,H) = 7.6 Hz, 2H, Ph), 6.87 (t, *J*(H,H) = 7.6 Hz, 2H, Ph), 5.10 (m, 4H, OCH_2, C*H*Ph), 4.57 (m, 2H, OCH_2), 3.18 (d, ^{3}J(H,P) = 10.0 Hz, 3H, POMe), 3.09 (d, ^{3}J(H,P) = 9.6 Hz, 3H, POMe) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2, 298 K): δ = 166.4 (s, OCN), 147.9 (s, $C^{2,6}$ C_5H_3N), 139.8 (s, C^{ipso} Ph), 137.5 (d, *J*(C,P) = 48.1 Hz,

C^{ipso} PPh), 135.8 (s, C^4 C_5H_3N), 130.9 (d, ^2J(C,P) = 11.1 Hz, PPh), 128.8, 128.4 (2*s*, Ph), 127.7 (d, ^2J(C,P) = 16.9 Hz, PPh), 127.6 (s, Ph), 126.7 (d, ^3J(C,P) = 8.6 Hz, PPh), 123.0 (s, $C^{3,5}$ C_5H_3N), 79.6 (s, OCH_2), 70.4 (s, *C*HPh), 52.6 (d, ^2J(C,P) = 5.0 Hz, POMe), 51.4 (d, ^2J(C,P) = 11.0 Hz, POMe) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 298 K): δ = 172.5 ppm. MS-ESI (*m/z*) = 733.9 $[RuCl_2(Ph\text{-}pybox)\{PPh(OMe)_2\}+Na]^+$ (40%), 710.9 $[RuCl_2(Ph\text{-}pybox)\{PPh(OMe)_2\}]^+$ (62%), 676.0 $[RuCl(Ph\text{-}pybox)\{PPh(OMe)_2\}]^+$ (100%). Elemental analysis calcd (%) for $C_{31}H_{30}Cl_2N_3O_4PRu$ (711.54 g/mol): C 52.33, H 4.25, N 5.91; found: C 52.16, H 4.58, N 5.69.

Synthesis of complex *trans*-[$RuCl_2$(MeCN){(*R*,*R*)-Ph-pybox}] (1m). A mixture of *trans*-[$RuCl_2(\eta^2\text{-}C_2H_4)$\{*(R*,*R*)-Ph-pybox}] (0.030 g, 0.05 mmol) and acetonitrile (0.312 mmol) in dichloromethane (5 mL) was heated at 55 ºC in a sealed tube for 6 h. Then, the solution was concentrated to ca. 2 mL and *n*-hexane (30 mL) was added affording a dark pink solid. The solvent was decanted and the resulting solid washed with *n*-hexane (3 x 5 mL) and vacuum-dried. Yield 90 % (0.026 g). ^1H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 7.79 (m, 2H, $C^{3,5}$ C_5H_3N), 7.63 (m, 1H, C^4 C_5H_3N), 7.57 (m, 4H, Ph), 7.39 (m, 6H, Ph), 5.36 (m, 4H, OCH_2, C*H*Ph), 4.64 (m, 2H, OCH_2), 1.79 (br s, 3H, MeCN) ppm. ^{13}C $\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 298 K): δ = 167.4 (s, OCN), 151.6 (s, $C^{2,6}$ C_5H_3N), 138.2 (s, Me*C*N), 137.9 (s, C^{ipso} Ph), 129.0, 128.9 (2*s*, Ph), 128.2 (s, C^4 C_5H_3N), 128.0 (s, Ph), 122.9 (s, $C^{3,5}$ C_5H_3N), 78.4 (s, OCH_2), 69.4 (s, *C*HPh), 3.1 (s, *Me*CN) ppm. IR (KBr, cm^{-1}): ν(C≡N) 2277 (w). ESI-MS: *m/z* = 582.0 ($[RuCl_2(MeCN)(Ph\text{-}pybox)]^+$, 20 %), 506.2 ($[RuCl(Ph\text{-}pybox)]^+$, 50 %), 470.3 ($[Ru(Ph\text{-}pybox)]^+$, 100%).

Synthesis of complexes *trans*-[$RuCl_2$(L){(*S*,*S*)-^{i}Pr-pybox}] (L = $PPh_2(OMe)$ (2h), $PPh_2(OEt)$ (2i), $PPh(OMe)_2$ (2j)). To a solution of complex *trans*-[$RuCl_2(\eta^2\text{-}C_2H_4)$\{(*S*,*S*)-^{i}Pr-pybox}] (**2a**) (0.1 g, 0.20 mmol) in dichloromethane (30 mL) the corresponding phosphonite or phosphinite (0.2 mmol) was added and the mixture

heated under reflux during 1 h 45 min. The solvent was then evaporated under reduced pressure and the solid residue was purified by chromatography over silica gel. Elution with a mixture of dichloromethane/methanol (50:1) gave a dark pink band from which the corresponding complexes **2h-2j** were isolated by solvent removal.

*Complex **2h***. Color: Dark pink. Yield 70 % (0.096 g). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 8.23 (m, 2H, PPh), 7.89 (m, 3H, H^4 C_5H_3N, PPh), 7.77 (d, J(H,H) = 8.0 Hz, 2H, H^{3,5} C_5H_3N), 7.50 (m, 6H, PPh), 4.67 (m, 4H, OCH_2), 3.85 (m, 2H, C*H*^{i}Pr), 3.57 (d, ^{3}J(H,P) = 10.4 Hz, 3H, POMe), 2.13 (m, 2H, C*H*Me$_2$), 0.62 (m, 12H, CH*Me*$_2$) ppm. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K): δ = 164.3 (s, OCN), 148.0 (s, C^{2,6} C_5H_3N), 137.1 (d, J(C,P) = 30.2 Hz, C^{ipso} PPh), 136.3 (d, J(C,P) = 34.7 Hz, C^{ipso} PPh), 135.3 (s, C^4 C_5H_3N), 132.9 (d, ^{2}J(C,P)= 10.8 Hz, PPh), 132.1 (d, ^{2}J(C,P)= 9.0 Hz, PPh), 130.0, 129.1 (2*s*, PPh), 127.8 (d, ^{3}J(C,P) = 8.4 Hz, PPh), 127.5 (d, ^{3}J(C,P) = 8.3 Hz, PPh), 122.3 (s, C^{3,5} C_3H_5N), 71.1 (s, OCH_2), 70.7 (s, *C*H^{i}Pr), 54.6 (d, ^{2}J(C,P)= 12.7 Hz, POMe), 28.0 (s, *C*HMe$_2$), 18.9, 14.2 (2*s*, *C*H*Me*$_2$) ppm. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 298 K): δ = 143.5 ppm. MS-ESI (*m/z*) = 870.2 [RuCl(^{i}Pr-pybox){$PPh_2(OMe)$}$_2$]$^+$ (23 %), 712.2 [$RuCl_2$(^{i}Pr-pybox){$PPh_2(OMe)$} + Na]$^+$ (15 %), 689.2 [$RuCl_2$(^{i}Pr-pybox){$PPh_2(OMe)$}]$^+$ (14%), 654.2 [RuCl(^{i}Pr-pybox){$PPh_2(OMe)$}]$^+$ (100%). Elemental analysis calcd (%) for $C_{30}H_{36}Cl_2N_3O_3PRu$ (689.58 g/mol): C 52.25, H 5.26, N 6.09; found: C 51.82, H 5.32, N 5.84.

*Complex **2i***. Color: Dark pink. Yield 75 % (0.105 g). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 8.25 (m, 2H, Ph), 7.87 (m, 3H, H^4 C_5H_3N, Ph), 7.78 (d, J(H,H) = 7.6 Hz, 2H, H^{3,5} C_5H_3N), 7.50 (m, 6H, Ph), 4.65 (m, 4H, C*H*^{i}Pr, OCH_2), 3.82 (m, 3H, OCH_2, $POCH_2$), 3.79 (m, 1H, $POCH_2$), 2.21 (m, 2H, C*H*Me$_2$), 1.31 (pt, J(H,H) = 6.8 Hz, 3H, CH_3), 0.62 (d, J(H,H) = 6.4 Hz, 6H, CH*Me*$_2$), 0.60 (d, J(H,H) = 7.2 Hz, 6H, CH*Me*$_2$) ppm. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K): δ = 164.3 (s, OCN), 148.1 (s, C^{2,6}

C_5H_3N), 137.6 (d, *J*(C,P) = 30.6 Hz, C^{ipso} PPh), 136.4 (d, *J*(C,P) = 34.5 Hz, C^{ipso} PPh), 135.2 (s, C^4 C_5H_3N), 132.9 (d, ^2J(C,P)= 11.1 Hz, PPh), 132.0 (d, ^2J(C,P) = 9.1 Hz, PPh), 129.9, 129.0 (2*s*, PPh), 127.9 (d, ^3J(C,P) = 9.0 Hz, PPh), 127.4 (d, ^3J(C,P) = 8.0 Hz, PPh), 122.2 (s, $C^{3,5}$ C_3H_5N), 71.0 (s, *C*H^{i}Pr), 70.6 (s, OCH_2), 63.6 (d, ^2J(C,P)= 13.1 Hz, $POCH_2$), 27.8 (s, *C*HMe_2), 18.8 (s, *C*H*Me*$_2$), 16.4 (d, ^3J(C,P) = 7.0 Hz, CH_3), 14.2 (s, *C*H*Me*$_2$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 298 K): δ = 141.2 ppm. MS-ESI (*m/z*) = 898.2 [RuCl(^{i}Pr-Pybox){PPh_2(OEt)}$_2$]$^+$ (26%), 726.2 [$RuCl_2$(^{i}Pr-Pybox){PPh_2(OEt)}+Na]$^+$ (21%), 668.3 [RuCl(^{i}Pr-Pybox){PPh_2(OEt)}]$^+$ (100%). Elemental analysis calcd (%) for $C_{31}H_{38}Cl_2N_3O_3PRu$ (703.61 g/mol): C 52.92, H 5.44, N 5.97; found: C 53.02, H 5.52, N 5.51.

*Complex **2j***. Color: Dark pink. Yield 86 % (0.111 g). ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 8.19 (m, 2H, PPh), 7.94 (t, *J*(H,H) = 7.8 Hz, 1H, H^4 C_5H_3N), 7.78 (d, *J*(H,H) = 7.8 Hz, 2H, $H^{3,5}$ C_5H_3N), 7.50 (m, 3H, PPh), 4.70 (m, 2H, OCH_2), 4.64 (m, 2H, OCH_2), 4.10 (d, ^3J(H,P) = 10.4 Hz, 3H, POMe), 3.69 (m, 2H, C*H*^{i}Pr), 3.63 (d, ^3J(H,P) = 9.6 Hz, 3H, POMe), 2.33 (m, 2H, C*H*Me_2), 0.71 (d, *J*(H,H) = 7.2 Hz, 6H, CH*Me*$_2$), 0.65 (d, *J*(H,H) = 6.8 Hz, 6H, CH*Me*$_2$) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 298 K): δ = 164.3 (s, OCN), 148.0 (s, $C^{2,6}$ C_5H_3N), 139.2 (d, *J*(C,P) = 46.3 Hz, C^{ipso} PPh), 135.9 (s, C^4 C_5H_3N), 131.5 (d, ^2J(C,P)= 12.2 Hz, PPh), 130.0 (s, PPh), 128.0 (d, ^3J(C,P) = 9.8 Hz, PPh), 122.5 (s, $C^{3,5}$ C_3H_5N), 71.0 (s, OCH_2), 70.9 (s, *C*H^{i}Pr), 53.2 (br s, POMe), 51.8 (d, ^2J(C,P) = 12.2 Hz, POMe), 27.9 (s, *C*HMe_2), 19.3, 14.6 (2*s*, *C*H*Me*$_2$) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 298 K): δ = 170.1 ppm. MS-ESI (*m/z*) = 666.2 [$RuCl_2$(^{i}Pr-pybox){PPh$(OMe)_2$}+Na]$^+$ (88%), 643.2 [$RuCl_2$(^{i}Pr-pybox){PPh$(OMe)_2$}]$^+$ (29%), 608.2 [RuCl(^{i}Pr-pybox){PPh$(OMe)_2$}]$^+$ (100%). Elemental analysis calcd (%) for $C_{25}H_{34}Cl_2N_3O_4PRu$ (643.51 g/mol): C 46.66, H 5.33, N 6.53; found: C 46.57, H 5.13, N 6.18.

Synthesis of complex *trans*-[$RuCl_2${$PPh_2(OEt)$}(indane-pybox}] (3i). To a solution of the complex *trans*-[$RuCl_2(\eta^2\text{-}C_2H_4)$(indane-pybox)] (0.076 g, 0.128 mmol) in dichloromethane (5 mL) was added an excess of $PPh_2(OEt)$ (42 μL, 0.192 mmol) and the mixture heated at 55 ºC in a sealed tube for 3 h. Once the reaction was completed, the solution was cooled at room temperature and then concetrated to ca. 2 mL. The residue was transferred to a silica gel chromatography column and eluted with a mixture of dichloromethane/methanol (100:1) to give a purple band. The evaporation of the solvents under reduced pressure and posterior addition of *n*-hexane (20 mL) afforded a purple solid. The solvent was decanted and the solid washed with *n*-hexane (3 x 5 mL) and vacuum-dried. Yield 47 % (0.048 g). ^{1}H NMR (400 MHz CD_2Cl_2, 298 K): δ = 8.38 (t, *J*(H,H) = 8.0 Hz, 2H, CH_{arom}), 8.22 (t, *J*(H,H) = 7.2 Hz, 2H, CH_{arom}), 7.80 (m, 2H, H^4 C_5H_3N, CH_{arom}), 7.69 (m, 1H, CH_{arom}), 7.51 (m, 9H, CH_{arom}), 7.23 (m, 3H, $H^{3,5}$ C_5H_3N, CH_{arom}), 7.00 (m, 2H, CH_{arom}), 5.79 (pt, *J*(H,H) = 6.0 Hz, 2H, CHO), 5.32 (d, *J*(H,H) = 6.0 Hz, 2H, CHN), 3.96 (m, 2H, $POCH_2$), 3.54 (d, *J*(H,H) = 18.0 Hz, 2H, CH_2), 3.45 (dd, *J*(H,H) = 18.0 Hz, *J*(H,H) = 6.0 Hz, 2H, OCH_2), 1.21 (t, *J*(H,H) = 7.2 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR (101 MHz CD_2Cl_2, 298 K): δ = 165.9 (s, OCN), 148.1 (s, $C^{2,6}$ C_5H_3N), 139.1, 138.4 (2s, C^{ipso} indane), 136.6 (d, *J*(C,P) = 29.9 Hz, C^{ipso} PPh), 135.4 (d, *J*(C,P) = 33.5 Hz, C^{ipso} Ph), 134.9 (s, C^4 C_5H_3N), 133.5 (d, ^{2}*J*(C,P) = 9.8 Hz, PPh), 133.4 (d, ^{2}*J*(C,P) = 10.6 Hz, PPh), 131.5, 131.4, 129.9, 129.7, 129.0, 128.9, 128.8, 128.7 (9*s*, CH_{arom}), 127.8 (d, ^{2}*J*(C,P) = 8.7 Hz, PPh), 127.4 (d, ^{3}*J*(C,P) = 8.5 Hz, PPh), 126.5 (s, CH_{arom}), 124.1 (s, $C^{3,5}$ C_5H_3N), 122.5 (s, CH_{arom}), 90.1 (s, CHO), 74.5 (CHN), 63.9 (d, ^{2}*J*(C,P) = 14.3 Hz, $POCH_2$), 37.3 (s, CH_2), 16.2 (s, CH_3) ppm. ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, 298 K): δ = 140.4 (s) ppm. ESI-MS: *m/z* = 760.2 ([RuCl{$PPh_2(OEt)$}(indane-pybox)]$^+$, 100 %). Elemental analysis calcd (%) for $C_{39}H_{34}Cl_2N_3O_3PRu$ (795.66): C 58.87, H 4.31, N 5.28; found: C 59.13, H 4.51, N 5.48.

Synthesis of complex *trans*-[$RuCl_2${$PPh(OMe)_2$}(indane-pybox)] (3j). To a solution of the complex *trans*-[$RuCl_2(\eta^2$-C_2H_4)(indane-pybox}] (0.090 g, 0.151 mmol) in dichloromethane (25 mL) was added $PPh(OMe)_2$ (24 μL, 0.151 mmol) and the mixture heated at 55 ºC in a sealed tube for 5 h. Once the reaction was completed, the solution was cooled at room temperature and then concentrated to ca. 2 mL. The residue was transferred to a silica gel chromatography column and eluted with a mixture of dichloromethane/methanol (100:1) to give a dark pink band. Then, the solvents were evaporated under reduced pressure and *n*-hexane (20 mL) was added affording a dark pink solid. The solvent was decanted and the solid washed with *n*-hexane (3 x 5 mL) and vacuum-dried. Yield 49 % (0.054 g). ^{1}H NMR (300 MHz CD_2Cl_2, 298 K): δ = 8.47 (m, 2H, CH_{arom}), 8.05 (d, *J*(H,H) = 7.5 Hz, 2H, CH_{arom}), 7.82 (m, 2H, CH_{arom}, H^4 C_5H_3N), 7.68 (d, *J*(H,H) = 7.8 Hz, 2H, $H^{3,5}$ C_5H_3N), 7.53 (m, 1H, CH_{arom}), 7.48 (m, 2H, CH_{arom}), 7.29-7.21 (m, 5H, CH_{arom}), 5.77 (pt, *J*(H,H) = 6.0 Hz, 2H, CHO), 5.06 (d, *J*(H,H) = 6.0 Hz, 2H, CHN), 4.24 (d, ^{3}*J*(H,P) = 10.2 Hz, 2H, POMe), 3.78 (m, 4H, POMe), 3.55 (d, *J*(H,H) = 18.0 Hz, 2H, CH_2), 3.44 (dd, *J*(H,H) = 18.0 Hz, *J*(H,H) = 6.0 Hz, 2H, CH_2) ppm. ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 298 K): δ = 165.9 (s, OCN), 147.9 (s, $C^{2,6}$ C_5H_3N), 139.2 (s, C^{ipso} indane), 138.4 (d, *J*(C,P) = 46.7 Hz, C^{ipso} PPh), 138.3 (s, C^{ipso} indane), 135.9 (s, C^4 C_5H_3N), 132.0 (d, ^{2}*J*(C,P) = 11.2 Hz, PPh), 130.2, 128.9 (2*s*, CH_{arom}), 127.7 (d, ^{3}*J*(C,P) = 8.5 Hz, PPh), 126.9, 124.2 (2*s*, CH_{arom}), 122.5 (s, $C^{3,5}$ C_5H_3N), 90.0 (s, CHO), 74.9 (CHN), 54.6 (d, ^{2}*J*(C,P) = 8.2 Hz, OMe), 52.1 (d, ^{2}*J*(C,P) = 11.9 Hz, OMe), 37.5 (s, CH_2) ppm. ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, 298 K): δ = 170.5 (s) ppm. ESI-MS: *m/z* = 758.1 ([$RuCl_2${$PPh(OMe)_2$}(indane-pybox)+Na]$^+$, 64 %), 735.2 ([$RuCl_2${$PPh(OMe)_2$}(indane-pybox)]$^+$, 19 %), 700.2 ([RuCl{$PPh(OMe)_2$}(indane-pybox)]$^+$, 100 %). Elemental analysis calcd (%) for

$C_{33}H_{30}Cl_2N_3O_4PRu \cdot 0.5\ CH_2Cl_2$ (778.05): C 51.72, H 4.02, N 5.40; found: 52.43 C, 4.09 H, 4.95 N.

Representative synthesis of amines 5 by catalytic hydrogenation reactions (procedure A). In a glovebox, a 2 mL vial was charged with imine **4a** (0.029 g, 0.15 mmol), **1j** (0.001 g, 1.5 μmol), ^{t}BuOK (50 μL, 0.15 M in Pr^{i}OH) and Pr^{i}OH (0.95 mL) and placed in a parallel pressure HEL CAT18 reactor. The reactor was purged three times with H_2, pressurized at 20 bar of H_2 and heated at 60 ºC for 24 h. The reactor was then allowed to cool down and slowly depressurized. The solution obtained was evaporated and conversion was determined by ^{1}H NMR of the resulting residue. This latter was purified by passing through a short pad of silica using a EtOAc/n-hexane (1:4) mixture as eluent. The resulting solution was evaporated under reduced pressure and the residue obtained analyzed by chiral HPLC to determine enantiomeric excess as described below. Alternatively, to remove unreacted imine, the residue obtained after the reaction can be dissolved in CH_2Cl_2 (2 mL), treated with 2 mL of HCl (2 mL, 2M) and the mixture stirred for 20 minutes. $NaHCO_3$ (satd, 3 mL) was added over the mixture, the organic layer extracted, dried over magnesium sulfate and concentrated. Enantiomeric excess was determined by chiral HPLC as detailed, racemic mixtures were prepared by a transfer hydrogenation reaction performed with the Shvo catalyst.[S9] With the exception of **5d**, all amines **5** are known compounds.

Representative synthesis of amines 5 using transfer hydrogenation reactions (procedure B). A reaction prepared in the glove-box (nitrogen filled) as described in Procedure A is placed in a tightly closed glass vial (2 mL), brought outside the glove-box and heated at 60 ºC for 24 h. Subsequently, and analogous work-up to that described above in procedure A was then followed to isolate the corresponding amine **5**.

Determination of enantiomeric excess and configuration of amines 5

Configuration for compounds **5a**, **5e**, **5h**, **5i**, **5j**, **5k**, **5l**, **5n**, and **5o** were determined by comparison of the optical rotation measurements with data reported in the literature. For compounds **5b**, **5d**, **5m** and **5p** were assigned by analogy.

***(S)-N*-phenyl-1-phenylethylamine (5a):**[S10] Colorless oil. Yield 87 % (0.026 g, procedure A). $[\alpha]^{D}_{20}$ = +4.1 (*c* 1.2, $CHCl_3$, 99 % ee). Lit. value:[S10c] $[\alpha]^{D}_{20}$ = -4.9 (*c* 1.0, $CHCl_3$, 97 % ee, *R* enantiomer). ^{1}H NMR (**(**$CDCl_3$, 300 MHz): δ = 7.38 (m, 4H, H arom), 7.27 (d, *J*(H,H) = 7.2 Hz, 1H, H arom), 7.13 (t, *J*(H,H) = 7.6 Hz, 2H, H arom), 6.68 (t, *J*(H,H) = 7.2 Hz, 1H, H arom), 6.55 (d, *J*(H,H) = 7.7 Hz, 2H, H arom), 4.52 (brm, 1H, C*H*CH_3), 4.06 (brs, 1H, NH), 1.55 (d, *J*(H,H) = 6.7 Hz, CH_3). ^{13}C{^{1}H} NMR **(**$CDCl_3$, 75 MHz): δ = 146.9 (C_q), 145.0 (C_q), 129.3 (2 CH arom), 128.8 (2 CH arom), 127.1 (CH arom), 126.1 (2 CH arom), 117.9 (CH arom), 113.9 (2 CH arom), 54.1 (*C*HCH_3), 24.9 (CH_3). HPLC: Chiralcel OJ-H, *n*-hexane-^{i}PrOH (93:7), flow 1.0 mL/min, λ = 243.8 nm, t_1 = 21.9 min (*R*), t_2 = 25.0 min (*S*).

***(S)-N*-phenyl-1-(*p*-fluorophenyl)ethylamine (5b):**[S11] Pale yellow oil. Yield 87 % (0.029 g, procedure B). $[\alpha]^{D}_{20}$ = +27.6 (*c* 1.1, $CHCl_3$, 99 % ee). Lit. value: [S11a] $[\alpha]^{D}_{20}$ = -24.8 (*c* 1.00, $CHCl_3$, 93 % ee, no configuration asigned). ^{1}H NMR **(**$CDCl_3$, 300 MHz): δ = 7.35 (dd, *J*(H,H) = 8.5 Hz, *J*(H,F) = 5.4 Hz, 2H, 2 H arom), 7.12 (t, *J*(H,H) = 7.9 Hz, 2H, 2 CH arom), 7.01 (t, *J*(H,H) = 8.7 Hz, 2H, 2 H arom), 6.71 (t, *J*(H,H) = 7.3 Hz, 1H, H arom), 6.55 (d, *J*(H,H) = 7.9 Hz, 2H, 2 H arom), 4.79 (vbr, NH), 4.48 (q, 1H, *J*(H,H) = 6.7 Hz, C*H*CH_3), 1.53 (d, *J*(H,H) = 6.8 Hz, 3H, CH_3) ppm. ^{13}C{^{1}H} NMR **(**$CDCl_3$, 100 MHz): δ = 161.9 (d, *J*(C,F) = 244 Hz, Cq), 146.8 (Cq), 140.7 (Cq), 129.3 (2 CH arom), 127.5 (d, *J*(C,F) = 8 Hz, 2 CH arom), 118.0 (CH arom), 115.6 (d, *J*(C,F) = 21 Hz, 2 CH arom), 113.9 (2 CH arom), 53.4 (*C*HCH_3), 25.1 (CH_3) ppm. HPLC:

Chiralcel OJ-H *n*-hexane-^{i}PrOH (99:1), flow 1.0 mL/min, λ = 241.4 nm, t_1 = 32.1 min (*S*), t_2 = 36.8 min (*R*). Configuration was determined by analogy with that observed in the hydrogenations of **4a**.

***N*-phenyl-1-(*p*-chlorophenyl)ethylamine (5c):**[S11a] Obtained with a 44 % conversion using procedure A. HPLC: Chiralcel OJ-H, *n*-hexane-^{i}PrOH (93:7), flow 1.0 mL/min, λ = 241.4 nm, t_1 = 12.6 min, t_2 = 13.8 min.

***(S)*-*N*-phenyl-1-(*m*-methoxyphenyl)ethylamine (5d):** Colorless oil. Yield 93 % (0.032 g, procedure B). $[\alpha]^{D}_{20}$ = +4.5 (*c* 1.4, $CHCl_3$, 99 % ee). HRMS (EI): *m/z* 227.1310, $[M]^+$ (exact mass calcd for $C_{15}H_{17}NO$: 227.1310). ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.27 (t, *J*(H,H) = 7.8 Hz, 1H, H arom), 7.12 (dd, *J*(H,H) = 8.5, 7.4 Hz, 2H, 2 H arom), 6.99 (d, *J*(H,H) = 7.6 Hz, 1H, H arom), 6.96 (m, 1H, H arom), 6.80 (dd, *J*(H,H) = 8.1, 2.4 Hz, 1H, H arom), 6.68 (t, *J*(H,H) = 7.3 Hz, 1H, H arom), 6.55 (d, *J*(H,H) = 8.6 Hz, 2H, 2 H arom), 4.48 (brm, 1H, $CHCH_3$), 4.04 (brs, 1H, NH), 3.81 (s, 3H, OCH_3), 1.53 (d, *J*(H,H) = 6.8 Hz, 3H, CHC*H*$_3$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ = 160.1 (Cq), 146.7 (2 Cq), 129.8 (2 CH arom), 129.2 (2 CH arom), 118.5 (CH arom), 118.1 (CH arom), 114.1 (CH arom), 112.4 (CH arom), 111.9 (CH arom), 55.3 (OCH_3), 54.4 (*C*HCH_3), 24.8 (CH*C*H$_3$) ppm. HPLC: Chiralpak AD-H *n*-hexane-^{i}PrOH (99:1), flow 1.0 mL/min, λ = 243.8 nm, t_1 = 10.5 min (*R*), t_2 = 12.1 min (*S*). Configuration was determined by analogy with that observed in the hydrogenations of **4a** and **4m**.

***(S)*-*N*-(*p*-methoxyphenyl)-1-phenylethylamine (5e):**[S11b, S12] Pale yellow oil. Yield 91 % (0.031 g, procedure B). $[\alpha]^{D}_{20}$ = -1.9 (*c* 1.3, $CHCl_3$, 99 % ee). Lit value:[S12] $[\alpha]^{D}_{20}$ = +1.9 (*c* 1, $CHCl_3$, 95 % ee, *R* enantiomer). ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 7.42 (d, *J*(H,H) = 7.3 Hz, 2H, 2 H arom), 7.37 (t, *J*(H,H) = 7.5 Hz, 2H, 2 H arom), 7.29 (d, *J*(H,H) = 5.9 Hz, 1H, H arom), 6.75 (d, *J*(H,H) = 8.9 Hz, 2H, 2 H arom), 6.53 (d, *J*(H,H) = 8.8 Hz, 2H, 2 H arom), 4.47 (q, *J*(H,H) = 6.7 Hz, 1H, C*H*CH_3), 3.84 (brs, 1H,

NH), 3.74 (s, 3H, OCH_3), 1.55 (d, *J*(H,H) = 6.7 Hz, 3H, $CHCH_3$) ppm. $^{13}C\{^1H\}$ NMR (**(**$CDCl_3$, 75 MHz): δ = 152.6 (Cq), 144.9 (Cq), 140.7 (Cq), 128.8 (2 CH arom), 127.1 (CH arom), 126.2 (2 CH arom), 115.4 (2 CH arom), 114.9 (2 CH arom), 55.9 (OCH_3), 55.1 ($CHCH_3$), 24.9 ($CHCH_3$) ppm. HPLC: Chiralpak AD-H *n*-hexane-^{i}PrOH (99:1), flow 1.0 mL/min, λ = 243.8 nm, t_1 = 13.0 min (*R*), t_2 = 14.2 min (*S*).

***(S)-N*-(*p*-Methoxyphenyl)-1-(*o*-methylphenyl)ethylamine (5h):**[S13a] Obtained by a modification of the general procedure A using imine **4h** (0.076 g, 0.32 mmol) **1j** (0.002 g, 0.003 mmol) and KO^{t}Bu (100 μL, 0.15 M in Pr^{i}OH) and Pr^{i}OH (0.75 mL) and heating at 70 ºC for 24 h. Pale yellow solid. Yield 91 % (0.070 g). $[\alpha]^D_{20}$ = +38.0 (*c* 2.2, MeOH, 99 % ee). Lit. value: [S14a] $[\alpha]^D_{22}$ = -33.5 (*c* 2.2, MeOH, 78 % ee, *R* enantiomer). ^1H NMR **(**$CDCl_3$, 500 MHz): δ = 7.48 (d, *J*(H,H) = 7.1 Hz, 1H, H arom), 7.17 (m, 3H, 3 H arom), 6.71 (m, 2H, 2 H arom), 6.47 (d, *J*(H,H) = 8.8 Hz, 2H, 2 H arom), 4.64 (q, *J*(H,H) = 6.6 Hz, 1H, $CHCH_3$), 3.72 (s, 3H, OCH_3), 2.43 (s, 3H, $ArCH_3$), 1.51 (d, *J*(H,H) = 6.6 Hz, 3H, $CHCH_3$) ppm. $^{13}C\{^1H\}$ NMR **(**$CDCl_3$, 125 MHz): δ = 152.0 (Cq), 142.9 (Cq), 141.4 (Cq), 134.6 (Cq), 130.6 (CH arom), 126.7 (CH arom), 126.6 (CH arom), 124.7 (CH arom), 114.8 (2 CH arom), 114.4 (2 CH arom), 55.8 (OCH_3), 50.6 ($CHCH_3$), 23.1 ($CHCH_3$), 19.0 (Ar-CH_3) ppm. HPLC: Chiracel OD-H *n*-hexane-^{i}PrOH (98:2), flow 1.0 mL/min, λ = 243.8 nm, t_1 = 7.7 min (*R*), t_2 = 9.9 min (*S*).

***(S)-N*-(*p*-Methoxyphenyl)-1-(*p*-methylphenyl)ethylamine (5i):**[S13] Pale yellow solid. Yield 91 % (0.033 g, procedure B). $[\alpha]^D_{20}$ = -21.4 (*c* 1.0, $CHCl_3$, 99 % ee). Lit. value: [S13c] $[\alpha]^D_{22}$ = +13.0 (*c* 1.0, $CHCl_3$, 99 % ee, *R* enantiomer). ^1H NMR **(**$CDCl_3$, 300 MHz): δ = 7.27 (d, *J*(H,H) = 7.9 Hz, 2H, 2 H arom), 7.15, (d, *J*(H,H) = 8.0 Hz, 2H, 2 H arom), 6.72 (d, *J*(H,H) = 8.9 Hz, 2H, 2 H arom), 6.55 (d, *J*(H,H) = 8.9 Hz, 2H, 2 H arom), 4.42 (q, *J*(H,H) = 6.6 Hz, 1H, $CHCH_3$), 3.81 (brs, NH; low intensity due to chemical exchange), 3.72 (s, 3H, OCH_3), 2.34 (s, 3H, $ArCH_3$), 1.53 (d, *J*(H,H) = 6.7 Hz, 3H,

CHC*H*$_3$) ppm. ^{13}C{^{1}H} NMR **(**$CDCl_3$, 100 MHz): δ = 152.5 (Cq), 141.9 (Cq), 140.8 (Cq), 136.7 (Cq), 129.4 (2CH arom), 126.1 (2 CH arom), 115.5 (2 CH arom), 114.9 (2 CH arom), 55.9 (OCH_3), 54.8 (*C*HCH_3), 24.9 (CH*C*H$_3$), 21.2 (Ar-CH_3) ppm. HPLC: Chiracel OD-H *n*-hexane-^{i}PrOH (99:1), flow 1.0 mL/min, λ = 243.8 nm, t_1 = 11.3 min (*R*), t_2 = 12.8 min (*S*).

***(S)-N*-(*p*-Methoxyphenyl)-1-(*o*-fluorophenyl)ethylamine (5j):**[S13a] Pale yellow oil**.** Yield 92 % (0.034 g, procedure A). $[\alpha]^D_{20}$ = -14.2 (*c* 1.0, $CHCl_3$, 99 % ee). Lit. value:[S14a] $[\alpha]^D_{22}$ = +8.4 (*c* 1.0, $CHCl_3$, 84 % ee, *R* enantiomer). ^{1}H NMR **(**$CDCl_3$, 400 MHz): δ = 7.42 (dt, *J*(H,H) = 7.6 Hz, *J*(H,F) = 1.7 Hz, 1H, H arom), 7.23 (m, 1H, H arom), 7.07 (m, 2H, 2 H arom), 6.73 (m, 2H, 2 H arom), 6.54 (d, *J*(H,H) = 8.7 Hz, 2H, 2 H arom), 4.79 (q, *J*(H,H) = 6.6 Hz, 1H, C*H*CH_3), 3.73 (s, 3H, OCH_3), 1.57 (d, *J*(H,H) = 6.6 Hz, 1H, CHC*H*$_3$) ppm. ^{13}C{^{1}H} NMR **(**$CDCl_3$, 100 MHz): δ = 160.5 (d, *J*(C,F) = 245 Hz, Cq), 152.3 (Cq), 140.7 (Cq), 131.7 (d, *J*(C,F) = 13 Hz, Cq), 128.3 (d, *J*(C,F) = 8 Hz, CH arom), 127.3 (d, *J*(C,F) = 5 Hz, CH arom), 124.4 (d, *J*(C,F) = 3 Hz, CH arom), 115.4 (d, *J*(C,F) = 22 Hz, CH arom), 114.8 (4 CH arom), 55.7 (OCH_3), 48.5 (*C*HCH_3), 23.3 (CH*C*H$_3$) ppm. HPLC: Chiracel OD-H *n*-hexane-^{i}PrOH (98:2), flow 0.5 mL/min, λ = 242.6 nm, t_1 = 15.6 min (*R*), t_2 = 18.1 min (*S*).

***(S)-N*-(*p*-Methoxyphenyl)-1-(*p*-trifluoromethylphenyl)ethylamine (5k):**[S14] Pale yellow solid. Yield 99 % (0.044 g, procedure B). $[\alpha]^D_{20}$ = +6.6 (*c* 0.5, $CHCl_3$, 99 % ee). Lit value:[S14] $[\alpha]^D$ = +6.5 (*c* 1.0, $CHCl_3$; 92 % ee, *S* enantiomer). ^{1}H NMR **(**$CDCl_3$, 500 MHz): δ = 7.59 (d, *J*(H,H) = 8.1 Hz, 2H, 2 H arom), 7.50 (d, *J*(H,H) = 8.1 Hz, 2H, 2 H arom), 6.72 (d, *J*(H,H) = 8.9 Hz, 2H, 2 H arom), 6.45 (d, *J*(H,H) = 8.9 Hz, 2H, 2 H arom), 4.48 (brm, 1H, C*H*CH_3), 3.83 (brs, 1H, NH), 3.71 (s, 3H, OCH_3), 1.52 (d, *J*(H,H) = 6.8 Hz, 3H, CHC*H*$_3$) ppm. ^{13}C{^{1}H} NMR **(**$CDCl_3$, 100 MHz): δ = 152.7 (Cq), 149.3 (Cq), 140.4 (Cq), 129.4 (q, *J*(C,F) = 32 Hz, Cq), 126.6 (2 CH arom), 125.8 (2 CH

arom), 124.4 (q, *J*(C,F) = 72 Hz, CF_3), 115.3 (2 CH arom), 115.0 (2 CH arom), 55.8 (OCH_3), 54.8 (CH*C*H_3), 24.9 (CH*C*H_3) ppm. HPLC: Chiracel OD-H *n*-hexane-^{i}PrOH (99:1), flow 1.0 mL/min, λ = 241.4 nm, t_1 = 32.0 min (*R*), t_2 = 42.0 min (*S*).

***(S)-N*-(*p*-methoxyphenyl)-1-(*m*-methoxyphenyl)ethylamine (5l):**[S10c, S13a, S15] Pale yellow oil. Yield 98 % (0.038 g, procedure B). Alternatively, **4l** (1.53 g, 6.00 mmol), **1j** (9.2 mg, 0.012 mmol), KO^{t}Bu (6.7 mg, 0.060 mmol) were dissolved in a Pr^{i}OH-toluene 1:1 mixture (3 mL) and pressurized under 20 bar H_2 at 60 ºC for 24 h. After the standard work-up, **5l** was obtained as a pale yellow oil (1.42 g, 92 % yield, 98 % ee). $[\alpha]^D_{20}$ = -6.8 (*c* 0.5, $CHCl_3$, 99 % ee). Lit value:[S15] $[\alpha]^D_{20}$ = +5.5 (*c* 1.05, $CHCl_3$, 72 % ee, *R* enantiomer). ^{1}H NMR **(**$CDCl_3$, 500 MHz): δ = 7.26 (t, *J*(H,H) = 7.9 Hz, 1H, H arom), 6.99 (d, *J*(H,H) = 7.6 Hz, 1H, H arom), 6.96 (s, 1H, H arom), 6.79 (dd, *J*(H,H) = 8.1, 2.4 Hz, 1H, H arom), 6.72 (d, *J*(H,H) = 8.8 Hz, 2H, 2 H arom), 6.50 (d, *J*(H,H) = 8.8 Hz, 2H, 2 H arom), 4.41 (brm, 1H, C*H*CH_3), 3.80 (s, 4H, OCH_3 + NH), 3.72 (s, 3H, OCH_3), 1.52 (d, *J*(H,H) = 6.7 Hz, 3H, CHC*H*$_3$) ppm. ^{13}C{^{1}H} NMR **(**$CDCl_3$, 100 MHz): δ = 160.0 (Cq), 152.4 (Cq), 147.1 (Cq), 141.0 (Cq), 129.8 (CH arom), 118.5 (CH arom), 115.2 (2 CH arom), 114.9 (2 CH arom), 112.3 (CH arom), 111.9 (CH arom), 55.8 (OCH_3), 55.3 (OCH_3), 54.9 (*C*HCH_3), 24.9 (CH*C*H_3) ppm. HPLC: Chiralcel OD-H *n*-hexane-^{i}PrOH (97:3), flow 1.0 mL/min, λ = 243.8 nm, t_1 = 12.3 min (*R*), t_2 = 14.2 min (*S*).

***(S)-N*-(*p*-methoxyphenyl)-1-(*m,p*-dimethoxyphenyl)ethylamine (5m):**[S13c, S15] White solid. Yield 65 % (0.028 g, procedure B). $[\alpha]^D_{20}$ = -7.3 (*c* 1.2, $CHCl_3$, 99 % ee). Lit value:[S15] $[\alpha]^D_{20}$ = +8.3 (*c* 0.98, $CHCl_3$, 78 % ee, *R* enantiomer), $[\alpha]^D_{17}$ = -16.0 (*c* 0.72, $CHCl_3$, 98 % ee).[S13c] ^{1}H NMR **(**$CDCl_3$, 300 MHz): δ = 6.94 (s, 1H, H arom), 6.89 (d, *J*(H,H) = 9.1 Hz, 1H, H arom), 6.80 (d, *J*(H,H) = 8.2 Hz, 1H, H arom), 6.70 (d, *J*(H,H) = 8.8 Hz, 2H, 2 H arom), 6.55 (d, *J*(H,H) = 8.8 Hz, 2H, 2 H arom), 4.35 (q, *J*(H,H) =

6.7 Hz, 1H, C*H*CH_3), 3.86 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 1.52 (d, *J*(H,H) = 6.6 Hz, 3H, CHC*H*$_3$) ppm (NH signal not observed). $^{13}C\{^1H\}$ NMR (**(**$CDCl_3$, 100 MHz): δ = 152.8 (Cq), 149.3 (Cq), 148.1 (Cq), 140.5 (Cq), 137.4 (Cq), 118.2 (CH arom), 115.8 (2 CH arom), 114.8 (2 CH arom), 111.3 (CH arom), 109.4 (CH arom), 56.0 (2 OCH_3), 55.8 (OCH_3), 55.2 (*C*HCH_3), 24.7 (CH*C*H_3) ppm. HPLC: Chiralcel OD-H *n*-hexane-^{i}PrOH (90:10), flow 0.5 mL/min, λ = 236.7 nm, t_1 = 26.3 min (*R*), t_2 = 30.4 min (*S*). Configuration was determined by analogy with that observed in the hydrogenation of **4i**.

***(S)-N*-(*p*-methoxyphenyl)-2-naphthylethylamine (5n):**[S10c, S13a, S13c] Yellow solid. Yield 80 % (0.033 g, procedure A). $[\alpha]^D_{20}$ = -25.7 (*c* 0.6, $CHCl_3$, 99 % ee). Lit. value:[S13c] $[\alpha]^D_{20}$ = -17.5 (*c* 0.61, $CHCl_3$, 99 % ee, *S* enantiomer). ^1H NMR (**(**$CDCl_3$, 300 MHz): δ = 7.84 (m, 4H, 4 H arom), 7.55 (d, *J*(H,H) = 8.6 Hz, 1H, H arom), 7.46 (m, 2H, 2 H arom), 6.71 (d, *J*(H,H) = 8.9 Hz, 2H, 2 H arom), 6.59 (d, *J*(H,H) = 8.9 Hz, 2H, 2 H arom), 4.61 (q, (d, *J*(H,H) = 6.7 Hz, 1H, $CHCH_3$), 4.39 (vbr, NH), 3.70 (s, 3H, OCH_3), 1.62 (d, (d, *J*(H,H) = 6.7 Hz, 3H, CHC*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (**(**$CDCl_3$, 100 MHz): δ = 152.8 (Cq), 142.1 (Cq), 140.2 (Cq), 133.6 (Cq), 132.9 (Cq), 128.6 (CH arom), 128.0 (CH arom), 127.8 (CH arom), 126.2 (CH arom), 125.7 (CH arom), 124.9 (CH arom), 124.7 (CH arom), 115.9 (2 CH arom), 114.9 (2 CH arom), 55.8 (OCH_3), 55.7 (*C*HCH_3), 24.7 (CH*C*H_3) ppm. HPLC: Chiracel OD-H *n*-hexane-^{i}PrOH (99:1), flow 1.0 mL/min, λ = 225.0 nm, t_1 = 23.2 min (*R*), t_2 = 28.3 min (*S*).

***(S)-N*-(*p*-methoxyphenyl)-1-naphthylethylamine (5o):**[S16] Yellow solid. Yield 73 % (0.030 g, procedure A). $[\alpha]^D_{20}$ = +183.9 (*c* 1.5, $CHCl_3$, 99 % ee). Lit. value:[S16] -158.4 (*c* 0.87, $CHCl_3$, 84 % ee, *R* enantiomer). ^1H NMR (**(**$CDCl_3$, 300 MHz): δ = 8.17 (d, *J*(H,H) = 8.2 Hz, 1H, H arom), 7.92 (d, *J*(H,H) = 7.4 Hz, 1H, H arom), 7.76 (d, *J*(H,H) = 8.2 Hz, 1H, H arom), 7.73 (d, *J*(H,H) = 7.1 Hz, 1H, H arom), 7.54 (m, 2H, 2 H arom), 7.44

(t, *J*(H,H) = 7.6 Hz, 1H, H arom), 6.68 (d, *J*(H,H) = 9.0 Hz, 2H, 2 H arom), 6.52 (d, *J*(H,H) = 8.7 Hz, 2H, 2 H arom), 5.26 (q, *J*(H,H) = 6.5 Hz, 1H, C*H*CH_3), 4.71 (vbr, NH), 3.68 (s, 3H, OCH_3), 1.69 (d, *J*(H,H) = 6.6 Hz, 3H, CHC*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (**(**$CDCl_3$, 75 MHz): δ = 152.9 (Cq), 139.8 (Cq), 139.3 (Cq), 134.2 (Cq), 130.9 (Cq), 129.2 (CH arom), 127.7 (CH arom), 126.2 (CH arom), 126.0 (CH arom), 125.6 (CH arom), 122.9 (CH arom), 122.6 (CH arom), 115.8 (2 CH arom), 114.9 (2 CH arom), 55.8 (OCH_3), 51.2 (*C*HCH_3), 23.5 (CH*C*H_3) ppm. HPLC: Chiracel OD-H *n*-hexane-^{i}PrOH (99:1), flow 1.0 mL/min, λ = 223.8 nm, t_1 = 22.3 min (*R*), t_2 = 29.6 min (*S*).

***(S)-N*-(*p*-methoxyphenyl)-1-phenylpropylamine (5p):**[S13b, S17] Colorless oil. Yield 80 % (0.030 g, procedure A). $[\alpha]^D_{20}$ = -26.5 (*c* 1.4, $CHCl_3$, 99 % ee). Lit. value:[S17] $[\alpha]^D_{20}$ = -20.0 (*c* 2.1, $CHCl_3$, 92 % ee, no configuration assigned). ^1H NMR (**(**$CDCl_3$, 300 MHz): 7.37 (m, 4H, 4 H arom), 7.26 (m, 1H, 1 H arom), 6.71 (d, *J*(H,H) = 8.9 Hz, 2H, 2 H arom), 6.55 (d, *J*(H,H) = 8.9 Hz, 2H, 2 H arom), 4.59 (vbr, NH), 4.18 (t, (d, *J*(H,H) = 6.7 Hz, 1H, C*H*CH_2), 3.71 (s, 3H, OCH_3), 1.88 (m, 2H, CH_2), 0.95 (t, *J*(H,H) = 7.4 Hz, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (**(**$CDCl_3$, 75 MHz): δ = 152.9 (Cq), 142.9 (Cq), 140.1 (Cq), 128.6 (2 CH arom), 127.3 (CH arom), 127.0 (2 CH arom), 116.0 (2 CH arom), 114.8 (2 CH arom), 62.0 (*C*HCH_2), 55.8 (OCH_3), 31.1 (CH_2), 10.9 (CH_2CH_3) ppm. HPLC: Chiracel OD-H *n*-hexane-^{i}PrOH (99:1), flow 1.0 mL/min, λ = 243.8 nm, t_1 = 10.4 min (*R*), t_2 = 11.5 min (*S*). Configuration was determined by analogy with that observed in the hydrogenations of **4e**.

***N*-(*p*-methoxyphenyl)-1-(isopropyl)ethylamine (5s):**[S13b] Obtained with 33 % conv. Following procedure A. HPLC: Chiracel OD-H *n*-hexane-^{i}PrOH (99:1), flow 0.5 mL/min, t_1 = 13.1 min (*R*), t_2 = 14.6 min (*S*).

X-ray Diffraction

Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of hexane into a solution of the complexes **1d** and **3j** in dichloromethane. In both cases diffraction data were recorded on a Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu-Ka radiation (λ = 1.5418 Å). 909 images were collected at a 63 mm fixed crystal-detector distance, using the oscillation method, with 1º oscillation and variable exposure time per image (20–163) s (for **1d)** and 506 images were collected at a 62 mm fixed crystal-detector distance, using the oscillation method, with 1.3º oscillation and variable exposure time per image (42.5–240) s (for **3j**). Data collection strategy was calculated with the program CrysAlis Pro CCD.[S18] Data reduction and cell refinement was performed with the program CrysAlis Pro RED.[S18] An multi-scan absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[S18]

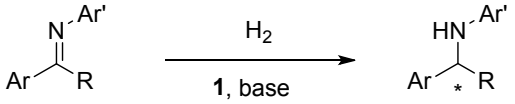
The software package WINGX[S19] was used for space group determination, structure solution and refinement. For **1d** the structure was solved by direct methods using SIR92.[S20] and for **3j** was solved by Patterson interpretation and phase expansion using DIRDIF.[S21]

In complex **3j** the asymmetric unit consists of two molecules. Also, highly disordered solvent molecules were found in the crystal which were impossible to refine using conventional discrete-atom models. To resolve these issues, the contribution of solvent electron density was removed by the SQUEEZE/PLATON.[S22]

Isotropic least-squares refinement on F^2 using SHELXL-2013[S23] was performed. During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined**.** The H atoms were geometrically located and their coordinates were refined riding on their parent atoms.

The function minimized was $([\Sigma wFo^2 - Fc^2)/\Sigma w(Fo^2)]^{1/2}$, where $w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$ (for **1d** $a = 0.0545$, $b = 6.9723$, for **3j** $a = 0.0671$, $b = 0.0$) with $\sigma(Fo^2)$ from counting statistics and $P = (\max(Fo^2, 0) + 2Fc^2)/3$. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[S24] The crystallographic plots were made with PLATON.[S21] CCDC 1558476 (**1d**) and CCDC 1558477 (**3j**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Hydrogenation of imines **4b-4n** with catalyst precursor **1d**[a]



R = Me (**5b**-**5o**), Et (**5p**)
Ar' = Ph (**5b**-**5d**), 4-MeO-Ph (**5e**-**5p**)

Entry	Cat.	Imine (Ar)	Conv[b]	% ee[c]
1	**1d**	**4b** (4-F-Ph)	92	98 (*S*)
2	**1d**	**4c** (4-Cl-Ph)	7	n. d.
3	**1d**	**4d** (3-MeO-Ph)	91	96 (*S*)
4	**1d**	**4e** (Ph)	98	99 (*S*)
5	**1d**	**4f** (4-Br-Ph)	<5	n. d.
6	**1d**	**4i** (4-Me-Ph)	67	98 (*S*)
7	**1d**	**4k** (4-CF_3-Ph)	>99	98 (*S*)
8	**1d**	**4l** (3-MeO-Ph)	>99	99 (*S*)
9	**1d**	**4m** (3,4-$(MeO)_2$-Ph)	54	97 (*S*)
10	**1d**	**4n** (2-naphthyl)	80	96 (*S*)
11	**1d**	**4o** (1-naphthyl)	9	n. d.
12	**1d**	**4p** (Ph)	29	n. d.

[a] Conditions: 20 bar H_2, 60 ºC, ^{i}PrOH, S/C/B = 100/1/5, [S] = 0.15 M, using KO^{t}Bu dissolved in ^{i}PrOH as a base, reaction time 24 h. [b] Conversion was determined by ^{1}H NMR, isolated yields for selected reactions in brackets. [c] Enantiomeric excess analyzed by HPLC (n. d. = not determined), configuration in brackets.

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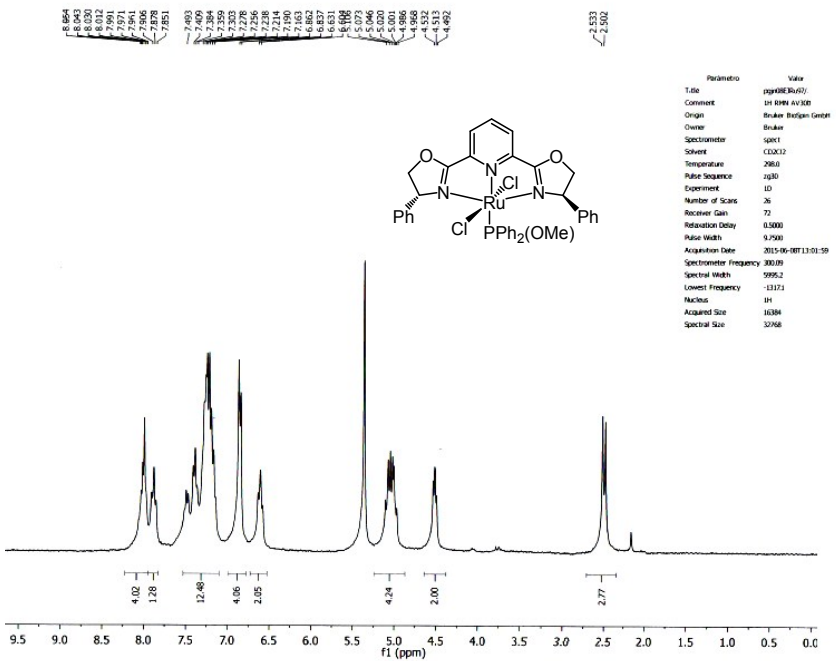
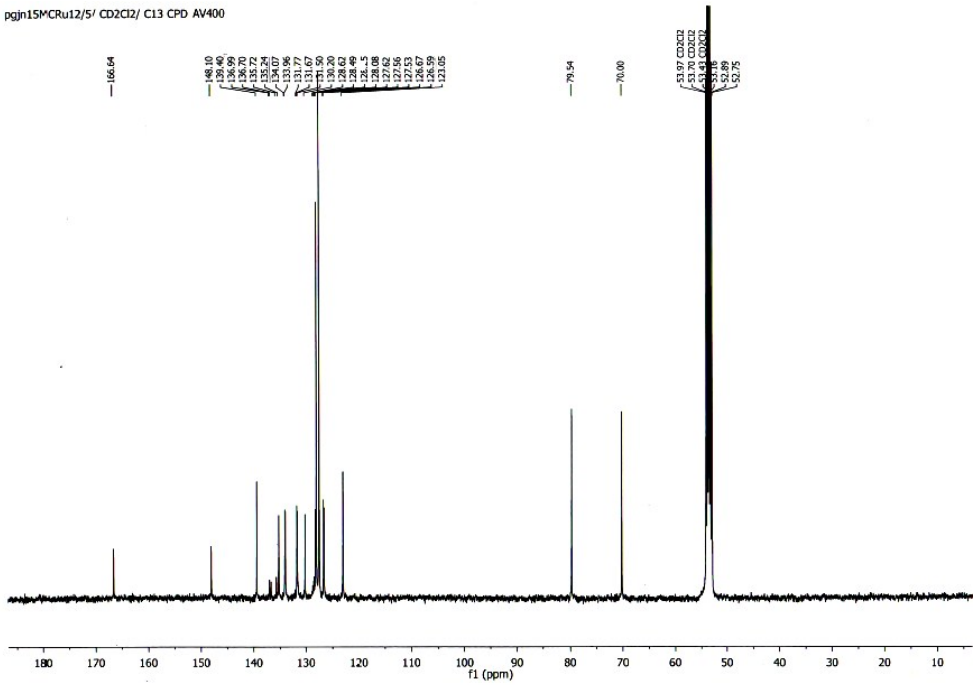
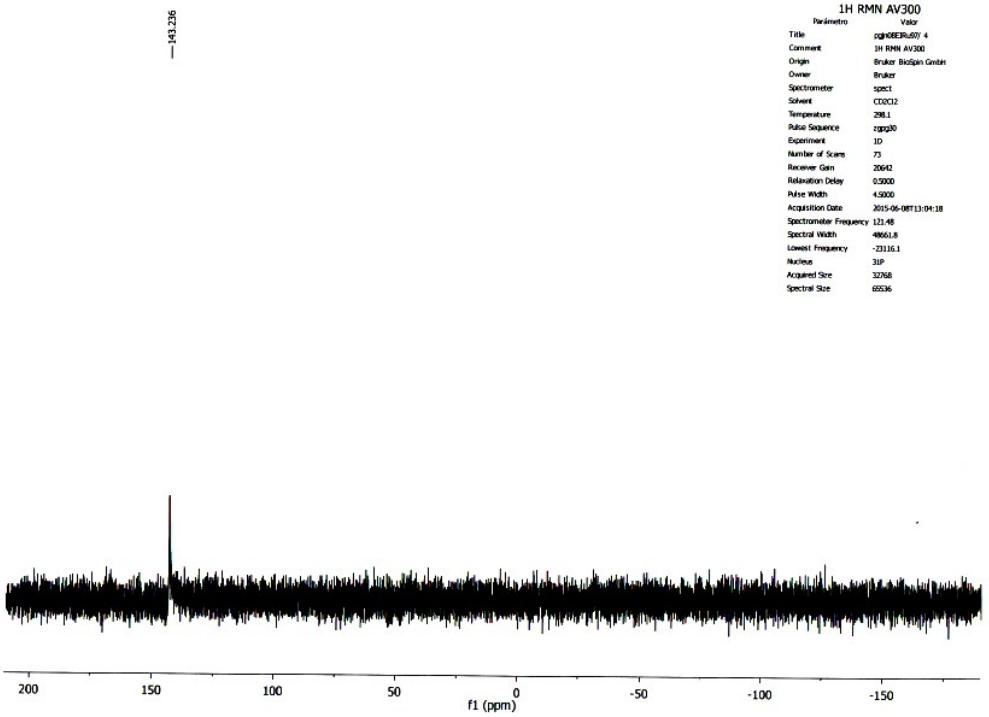


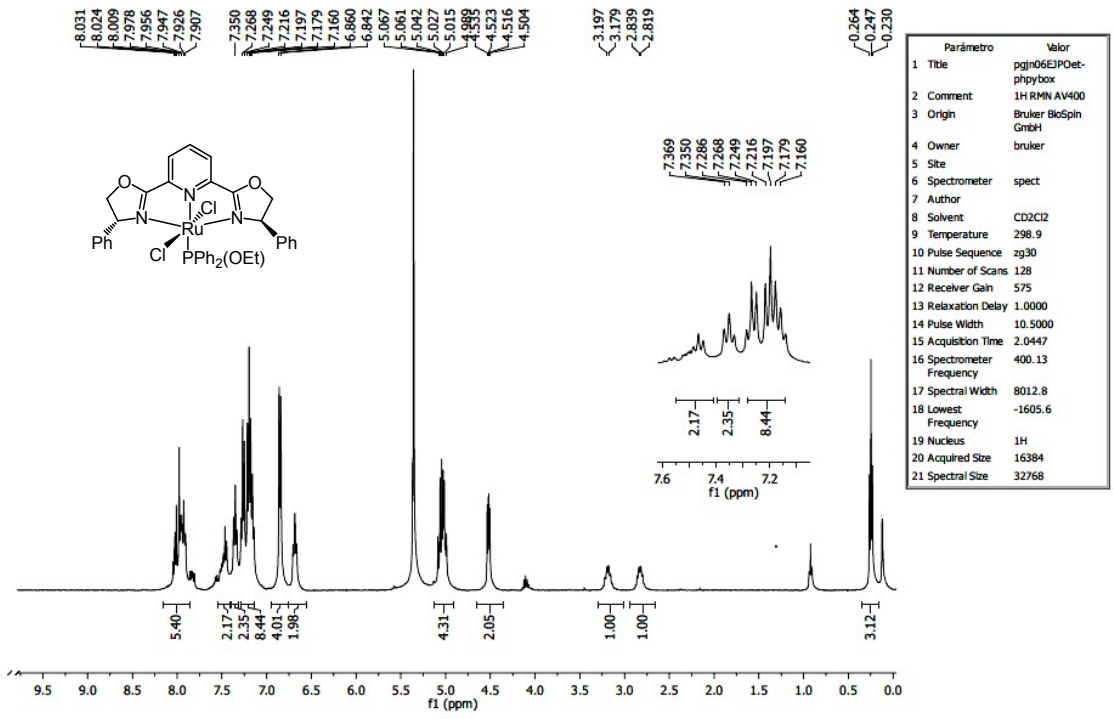
^{1}H NMR (300 MHz, CD_2Cl_2) of **1h**



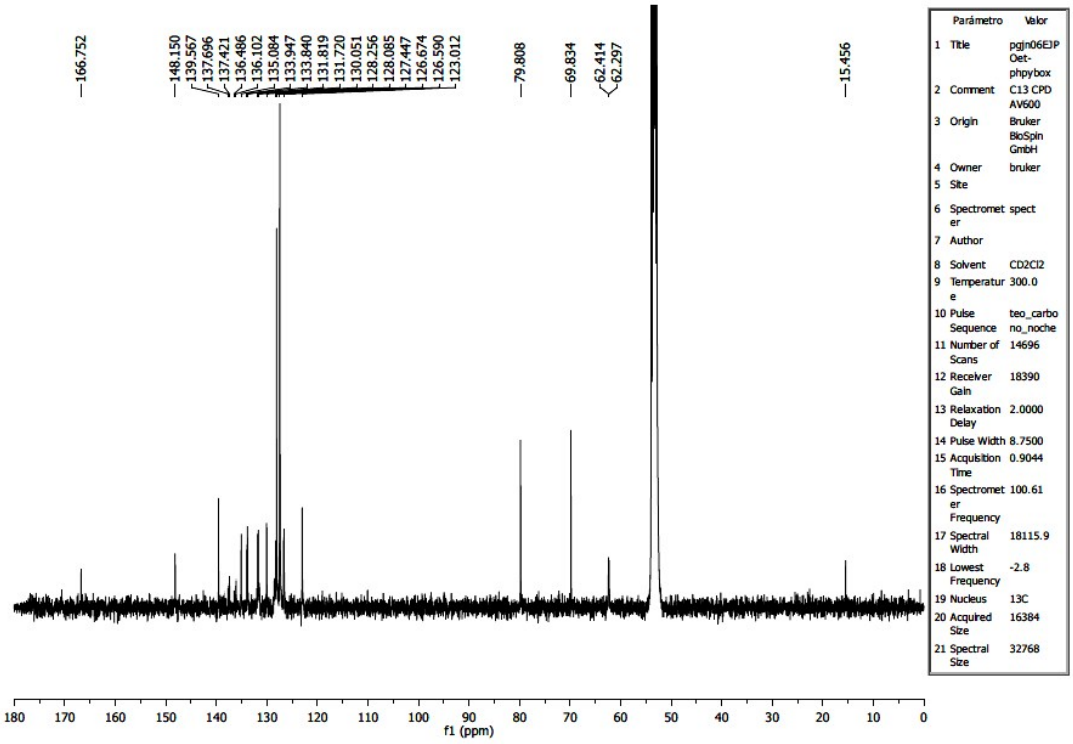
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) of **1h**



$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2) of **1h**



^{1}H NMR (400 MHz, CD_2Cl_2) of **1i**



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7	Author	
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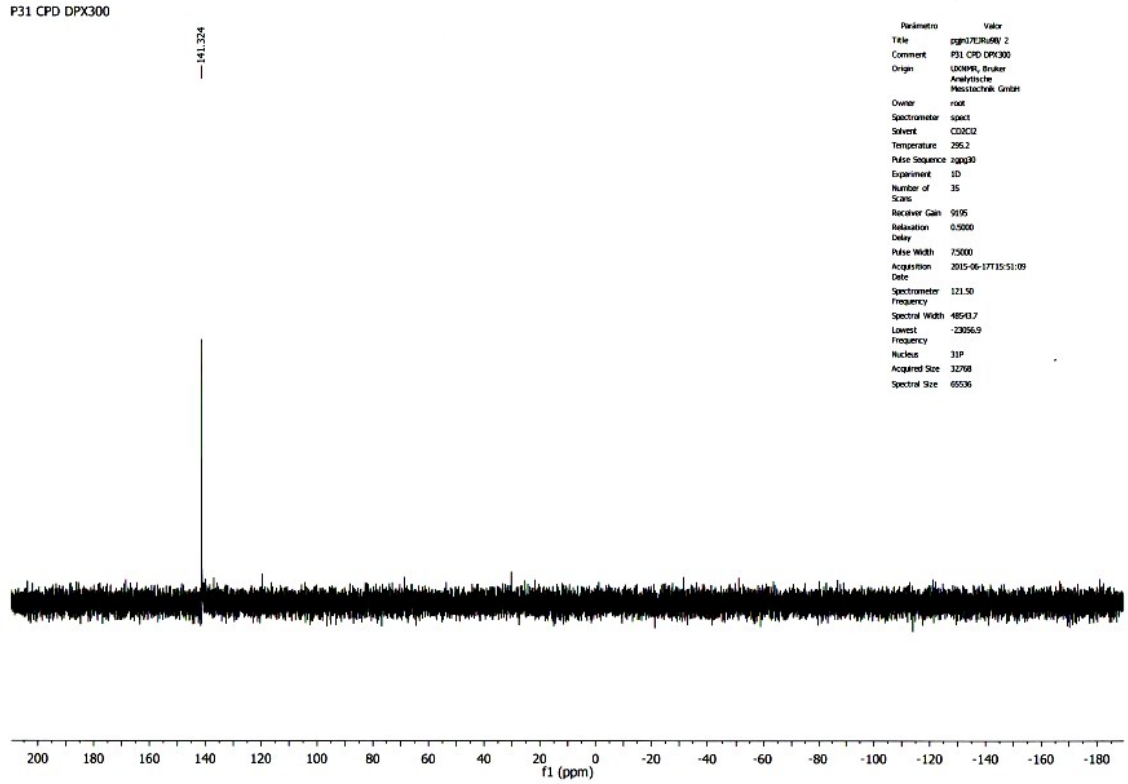
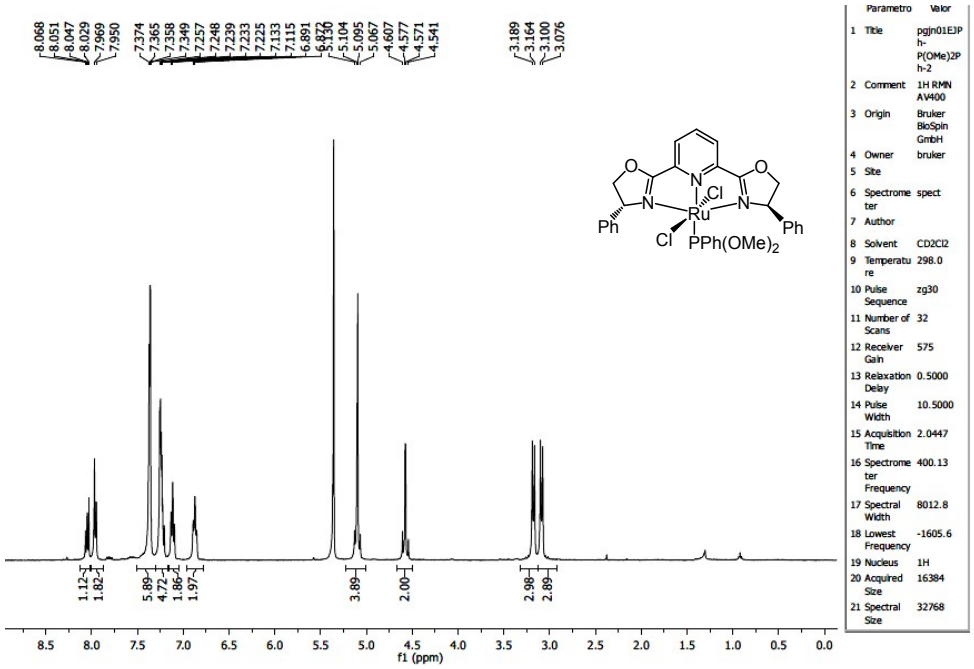
16	Spectrometer Frequency	100.61
17	Spectral Width	18115.9
18	Lowest Frequency	-2.8
19	Nucleus	13C
20	Acquired Size	16384
21	Spectral Size	32768

$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) of **1i**

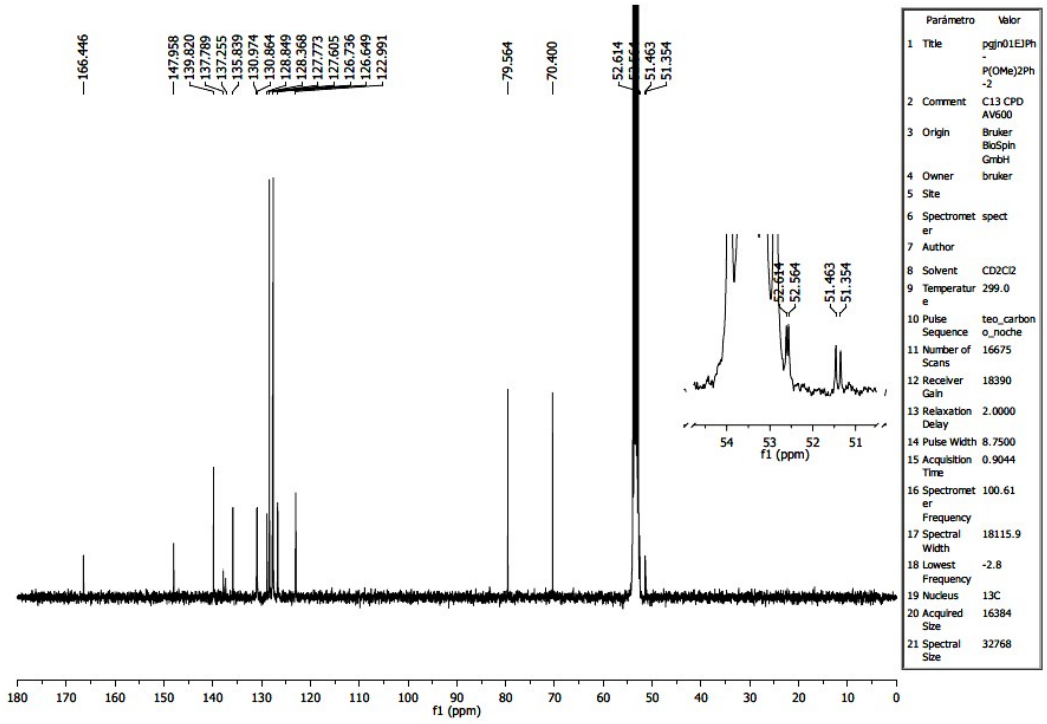


Parámetro	Valor
Title	pgjn17EJRu6BV 2
Comment	P31 CPD DPX300
Origin	LDCMPR, Bruker Analytische Messtechnik GmbH
Owner	root
Spectrometer	spect
Solvent	CD2Cl2
Temperature	295.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	35
Receiver Gain	9195
Relaxation Delay	0.5000
Pulse Width	75000
Acquisition Date	2015-06-17T15:51:09
Spectrometer Frequency	121.50
Spectral Width	48543.7
Lowest Frequency	-23056.9
Nucleus	31P
Acquired Size	32768
Spectral Size	65536

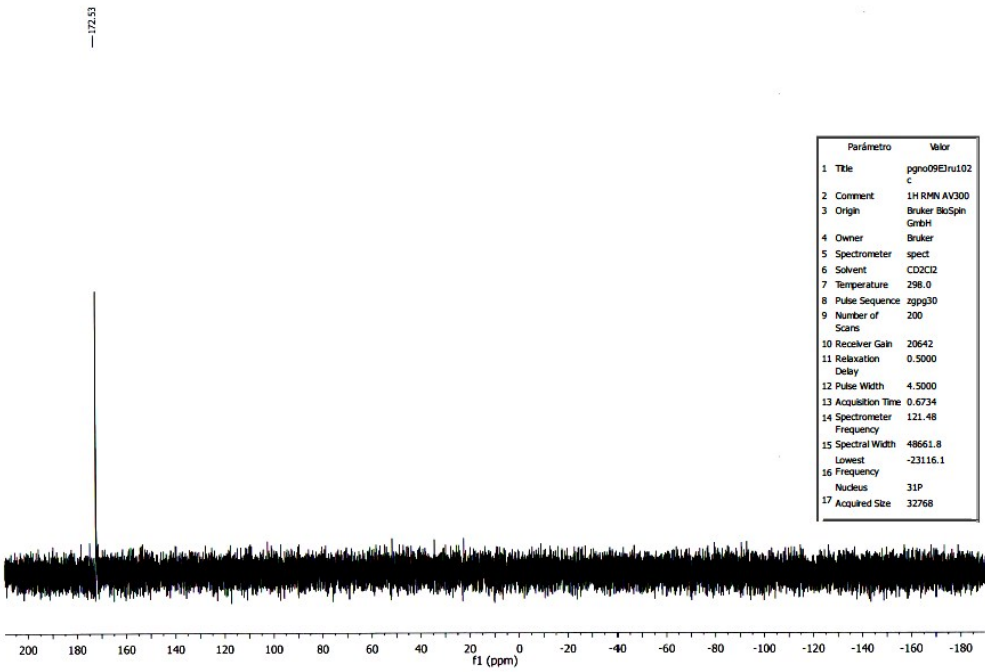
$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2) of **1i**



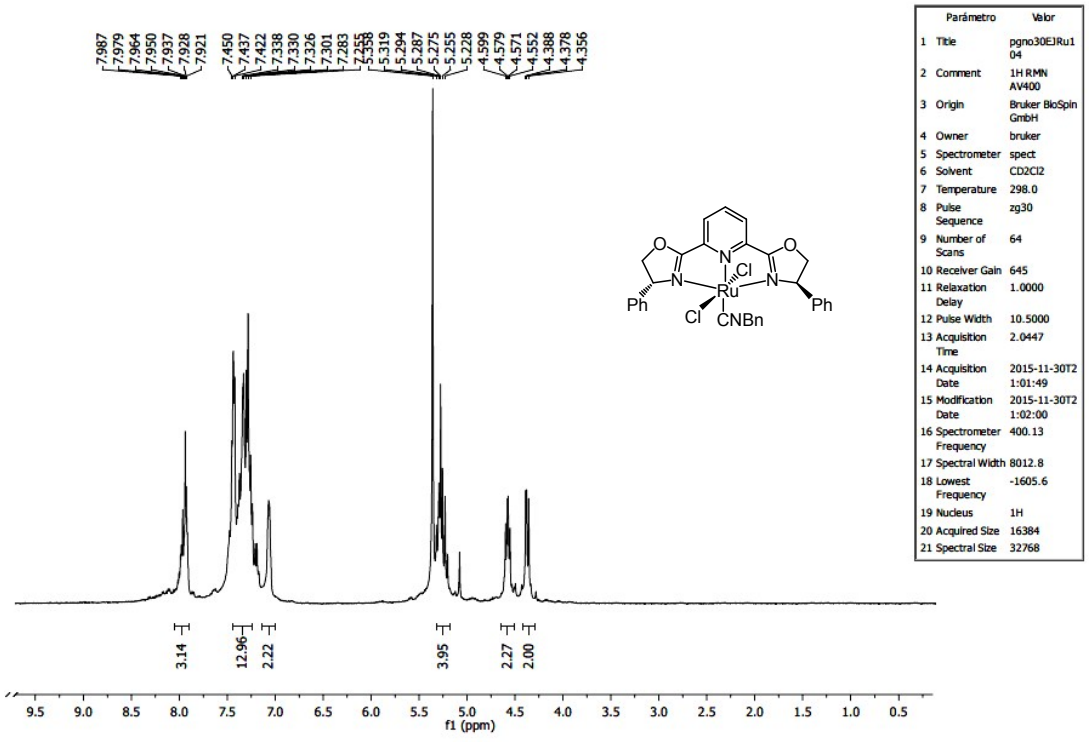
^{1}H NMR (400 MHz, CD_2Cl_2) of **1j**



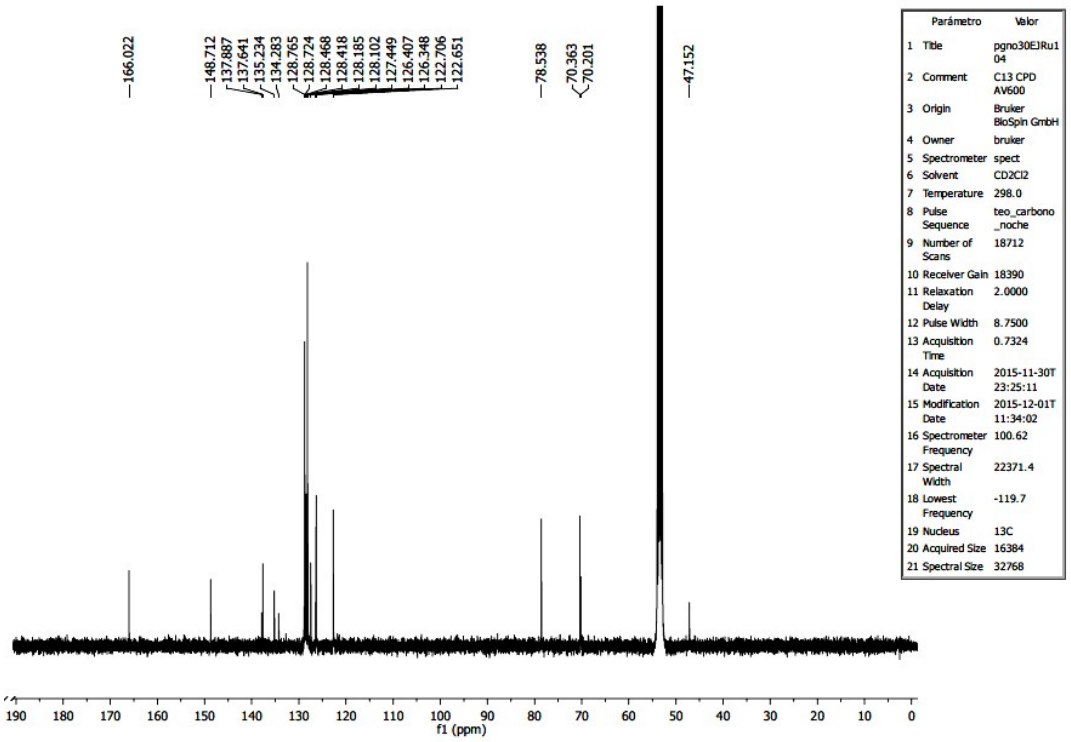
^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) of **1j**



$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2) of **1j**

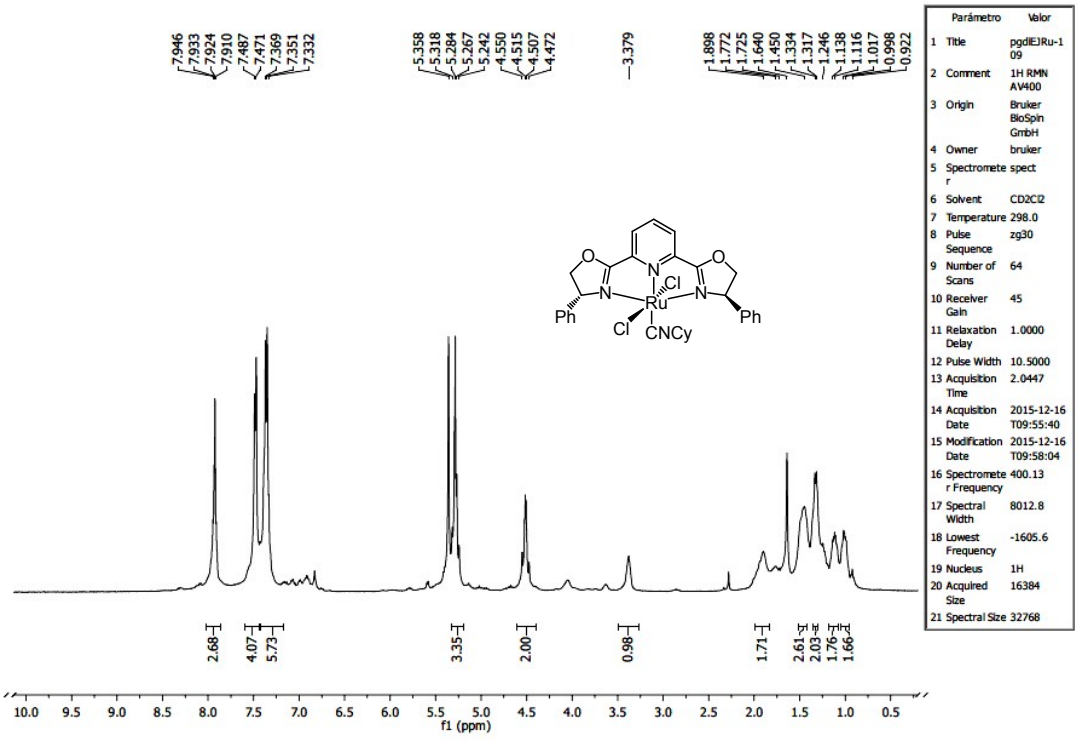


^{1}H NMR (400 MHz, CD_2Cl_2) of **1k**



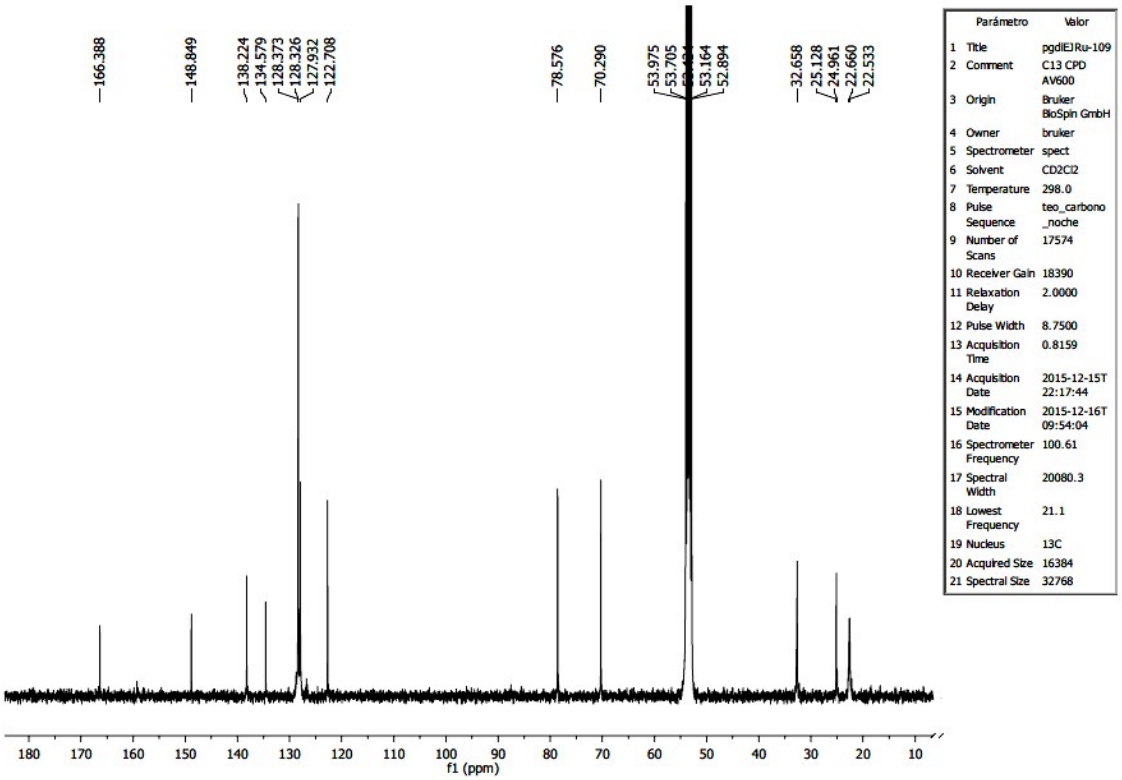
	Parámetro	Valor
1	Title	pgno30EJRu104
2	Comment	C13 CPD AV600
3	Origin	Bruker BioSpin GmbH
4	Owner	bruker
5	Spectrometer	spect
6	Solvent	CD2Cl2
7	Temperature	298.0
8	Pulse Sequence	teo_carbono_noche
9	Number of Scans	18712
10	Receiver Gain	18390
11	Relaxation Delay	2.0000
12	Pulse Width	8.7500
13	Acquisition Time	0.7324
14	Acquisition Date	2015-11-30T 23:25:11
15	Modification Date	2015-12-01T 11:34:02
16	Spectrometer Frequency	100.62
17	Spectral Width	22371.4
18	Lowest Frequency	-119.7
19	Nucleus	13C
20	Acquired Size	16384
21	Spectral Size	32768

$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2) of **1k**

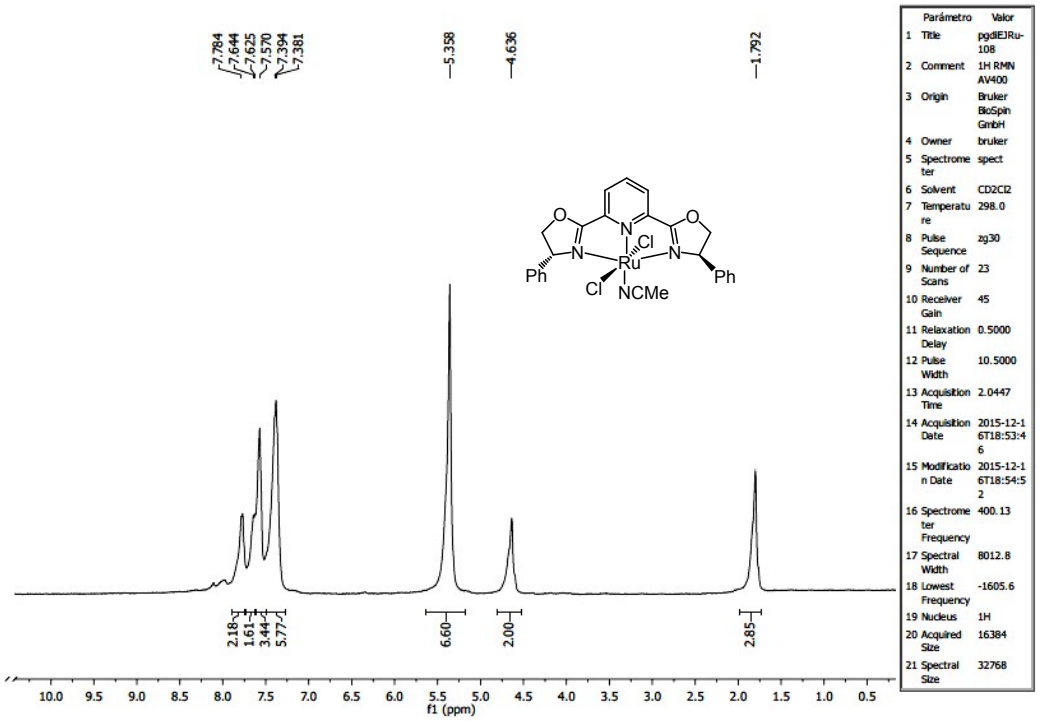


	Parámetro	Valor
1	Title	pgdlEJRu-109
2	Comment	1H RMN AV400
3	Origin	Bruker BioSpin GmbH
4	Owner	bruker
5	Spectrometer	spect r
6	Solvent	CD2Cl2
7	Temperature	298.0
8	Pulse Sequence	zg30
9	Number of Scans	64
10	Receiver Gain	45
11	Relaxation Delay	1.0000
12	Pulse Width	10.5000
13	Acquisition Time	2.0447
14	Acquisition Date	2015-12-16 T09:55:40
15	Modification Date	2015-12-16 T09:58:04
16	Spectrometer Frequency	400.13
17	Spectral Width	8012.8
18	Lowest Frequency	-1605.6
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

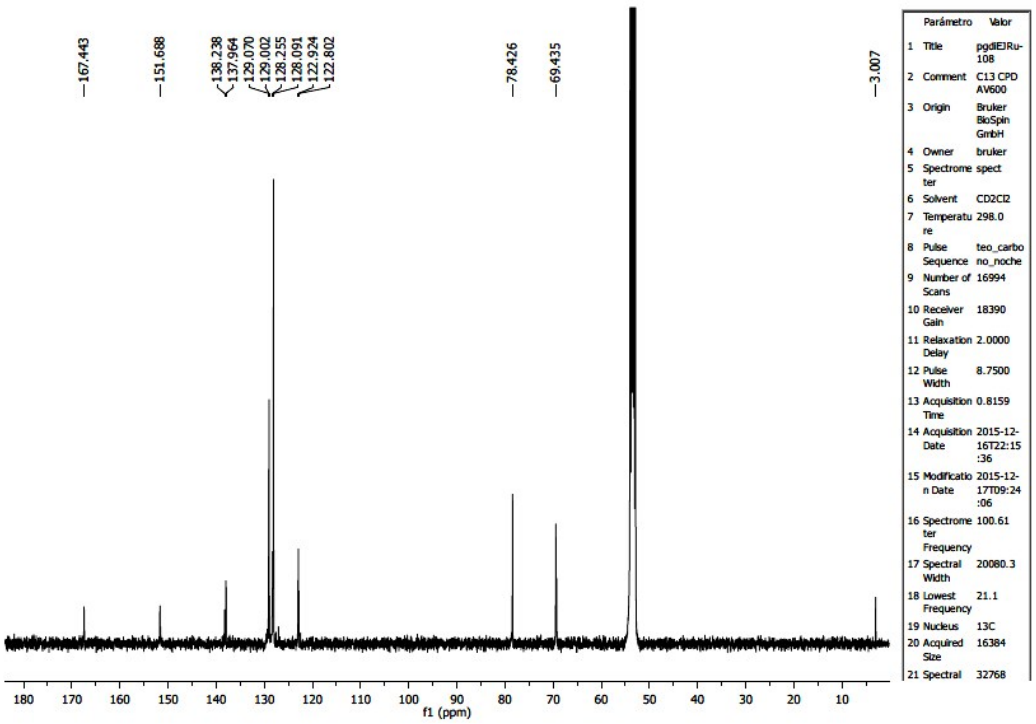
^{1}H NMR (400 MHz, CD_2Cl_2) of **1l**



$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2) of **1l**

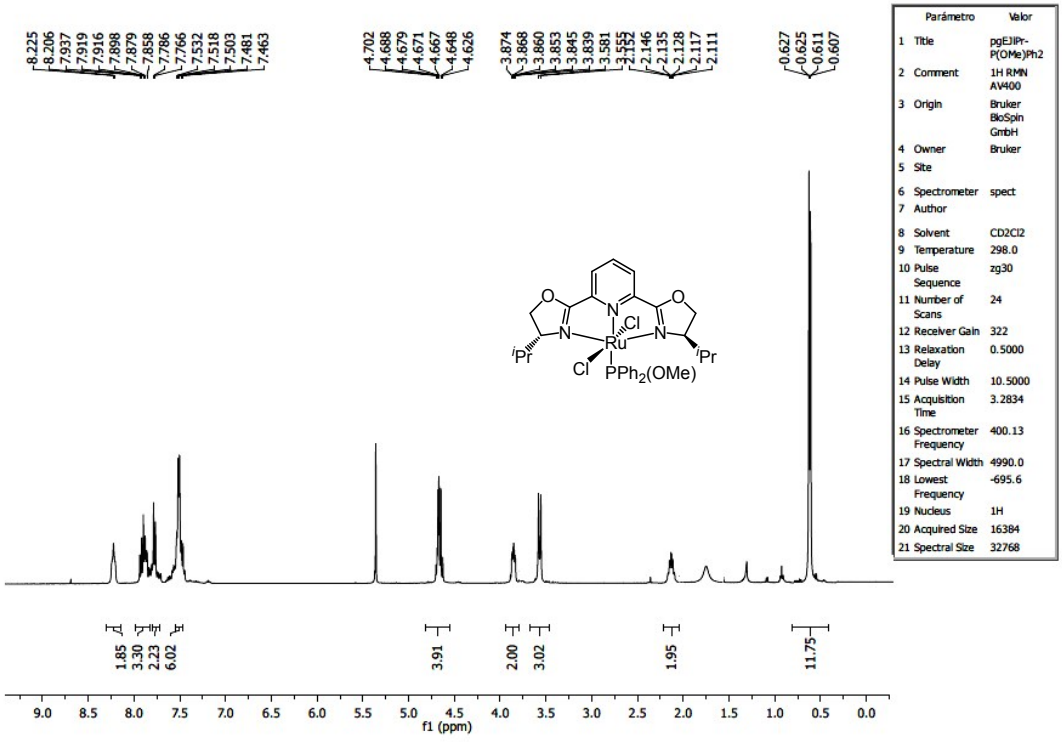


^{1}H NMR (400 MHz, CD_2Cl_2) of **1m**



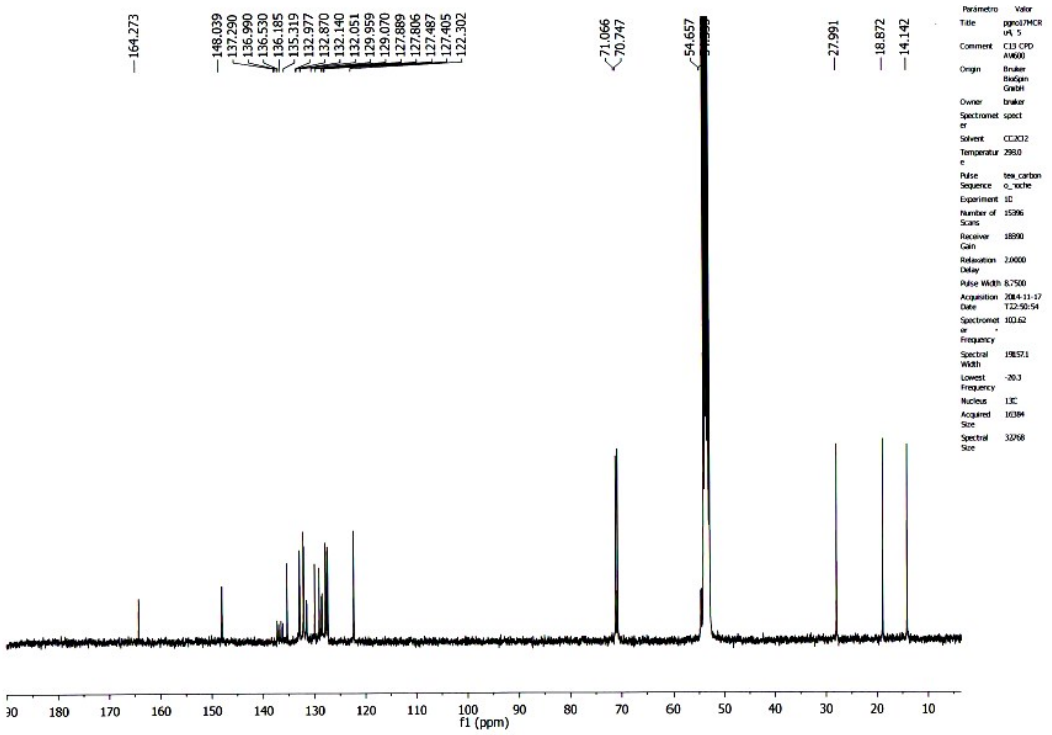
	Parámetro	Valor
1	Title	pgdlEJRu-108
2	Comment	C13 CPD AV600
3	Origin	Bruker BioSpin GmbH
4	Owner	bruker
5	Spectrometer	spect
6	Solvent	CD2Cl2
7	Temperature	298.0
8	Pulse Sequence	teo_carbono_noche
9	Number of Scans	16994
10	Receiver Gain	18390
11	Relaxation Delay	2.0000
12	Pulse Width	8.7500
13	Acquisition Time	0.8159
14	Acquisition Date	2015-12-16T22:15:36
15	Modification Date	2015-12-17T09:24:06
16	Spectrometer Frequency	100.61
17	Spectral Width	20080.3
18	Lowest Frequency	21.1
19	Nucleus	13C
20	Acquired Size	16384
21	Spectral	32768

$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2) of **1m**

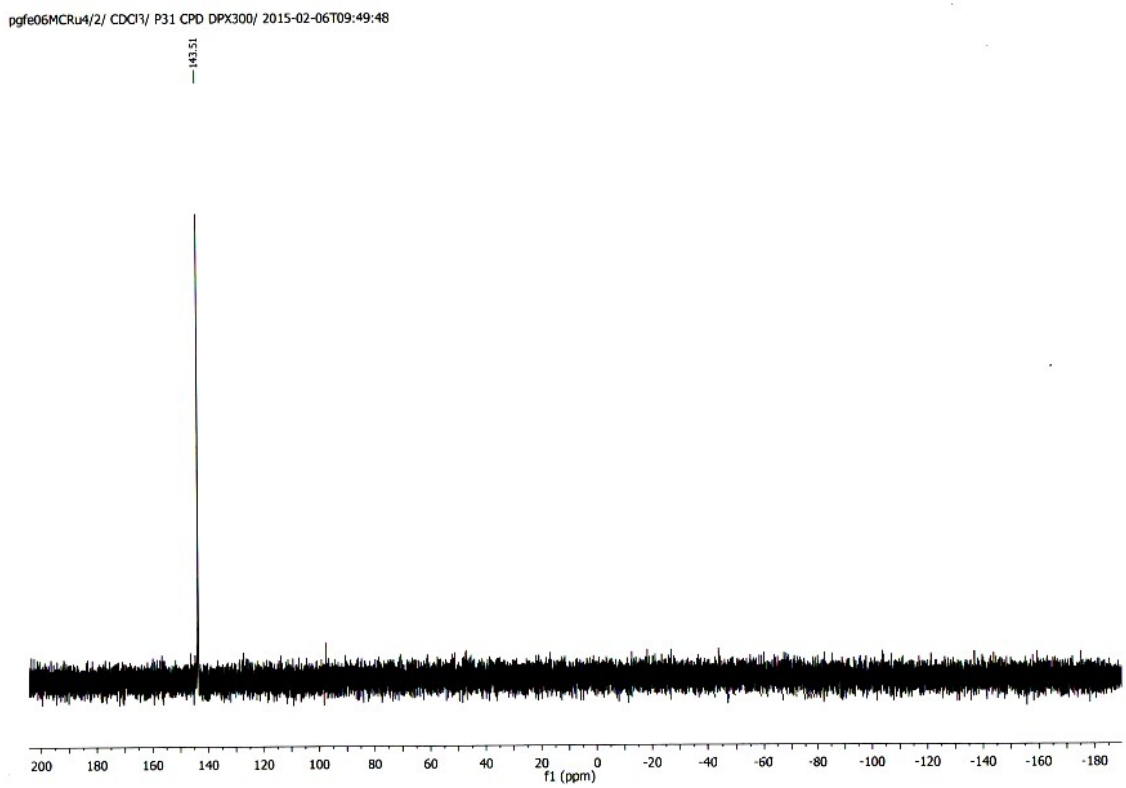


	Parámetro	Valor
1	Title	pgEJIPr-P(OMe)Ph2
2	Comment	1H RMN AV400
3	Origin	Bruker BioSpin GmbH
4	Owner	Bruker
5	Site	
6	Spectrometer	spect
7	Author	
8	Solvent	CD2Cl2
9	Temperature	298.0
10	Pulse Sequence	zg30
11	Number of Scans	24
12	Receiver Gain	322
13	Relaxation Delay	0.5000
14	Pulse Width	10.5000
15	Acquisition Time	3.2834
16	Spectrometer Frequency	400.13
17	Spectral Width	4990.0
18	Lowest Frequency	-695.6
19	Nucleus	1H
20	Acquired Size	16384
21	Spectral Size	32768

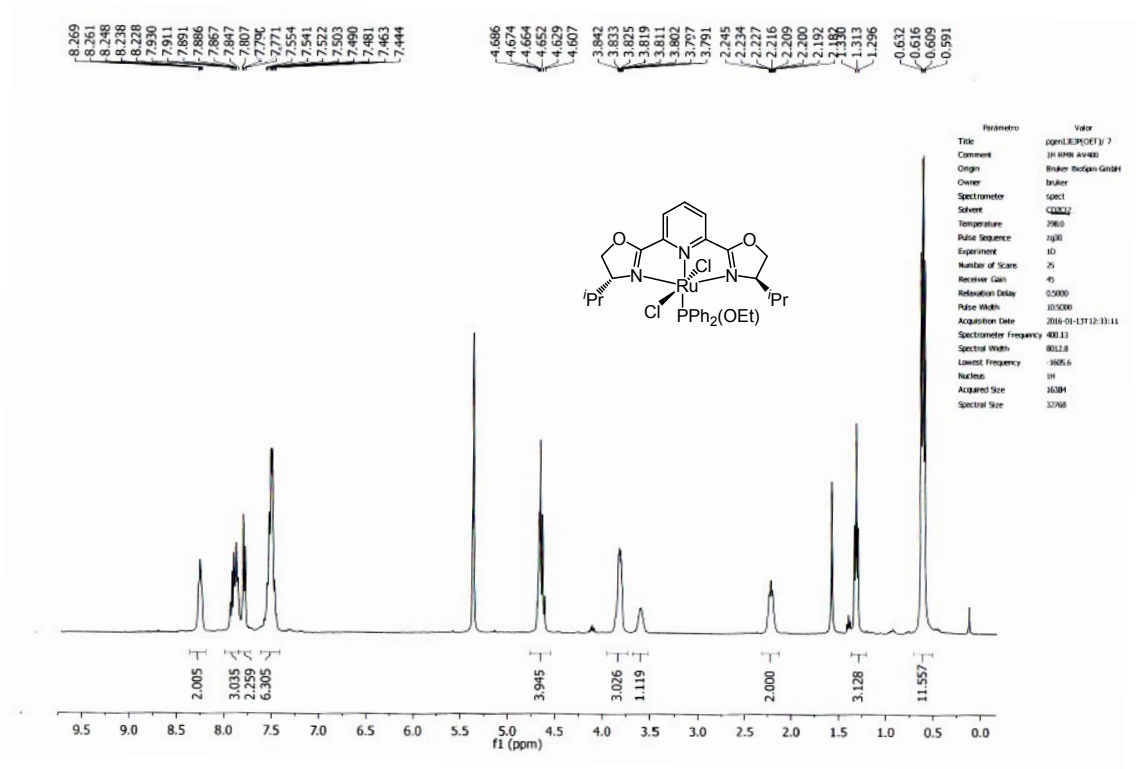
^{1}H NMR (400 MHz, CD_2Cl_2) of **2h**



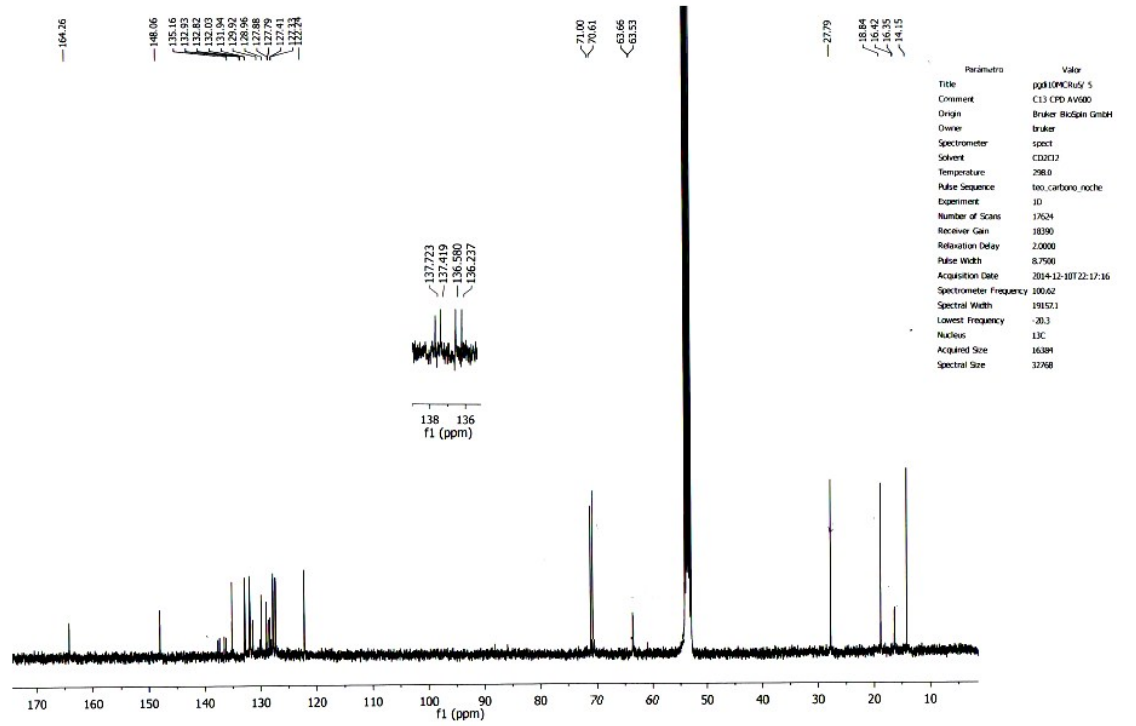
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) of **2h**



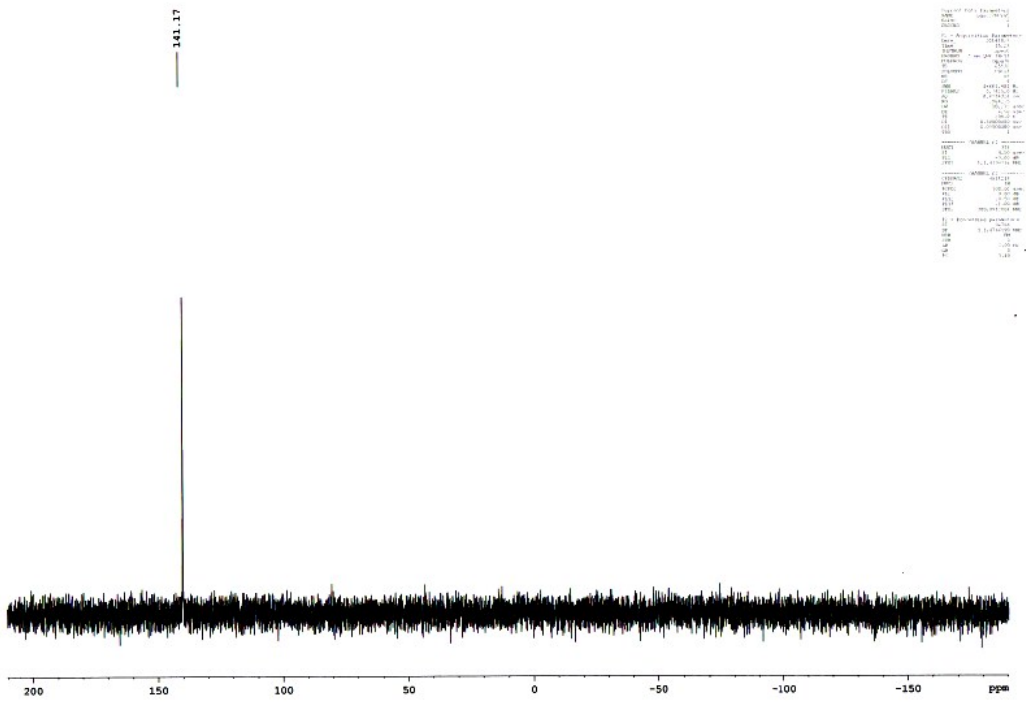
$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2) of **2h**



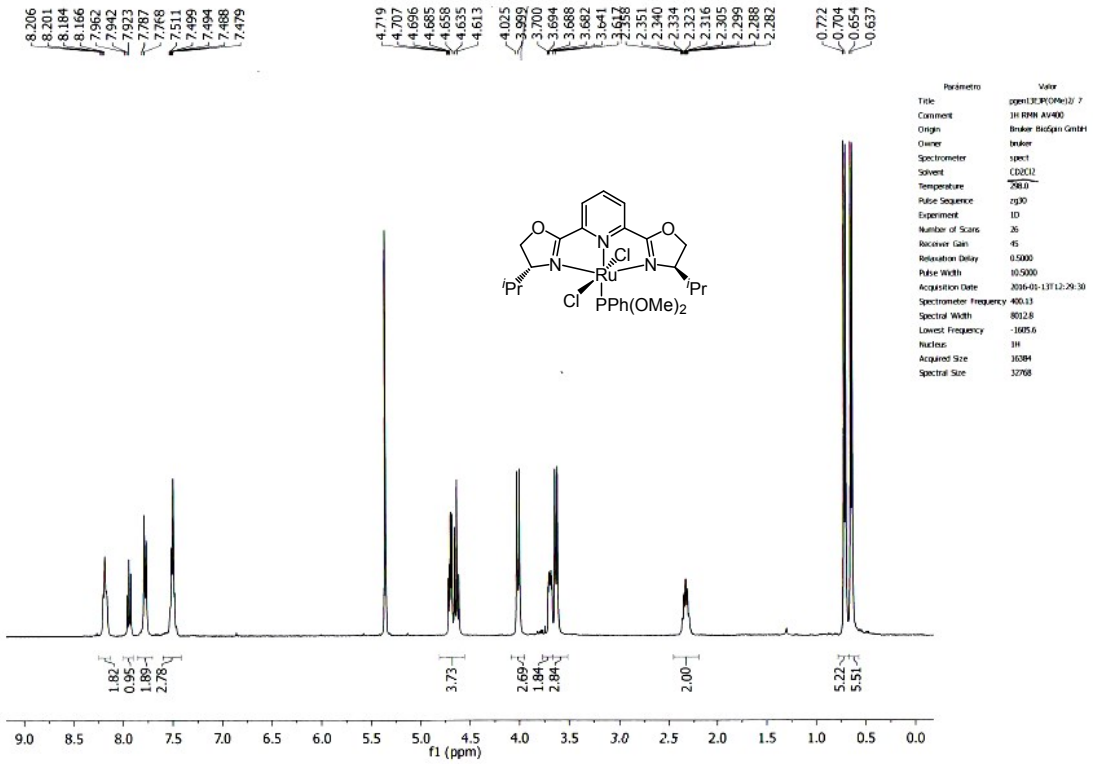
^{1}H NMR (400 MHz, CD_2Cl_2) of **2i**



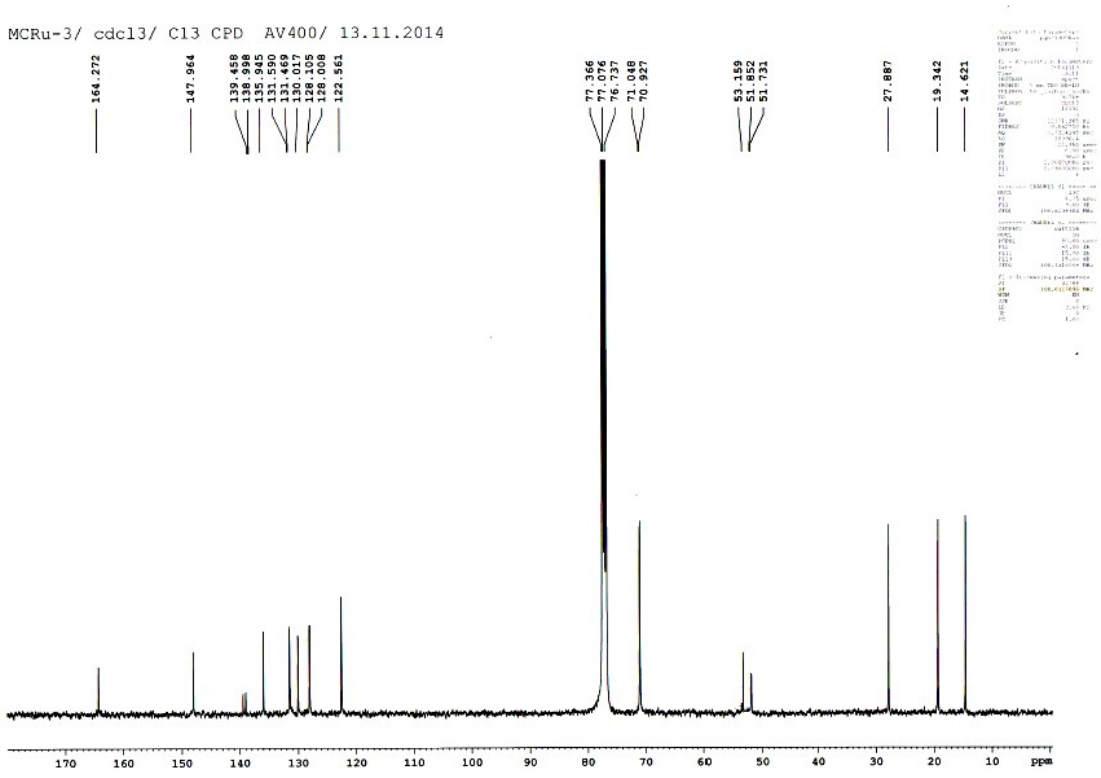
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2) of **2i**



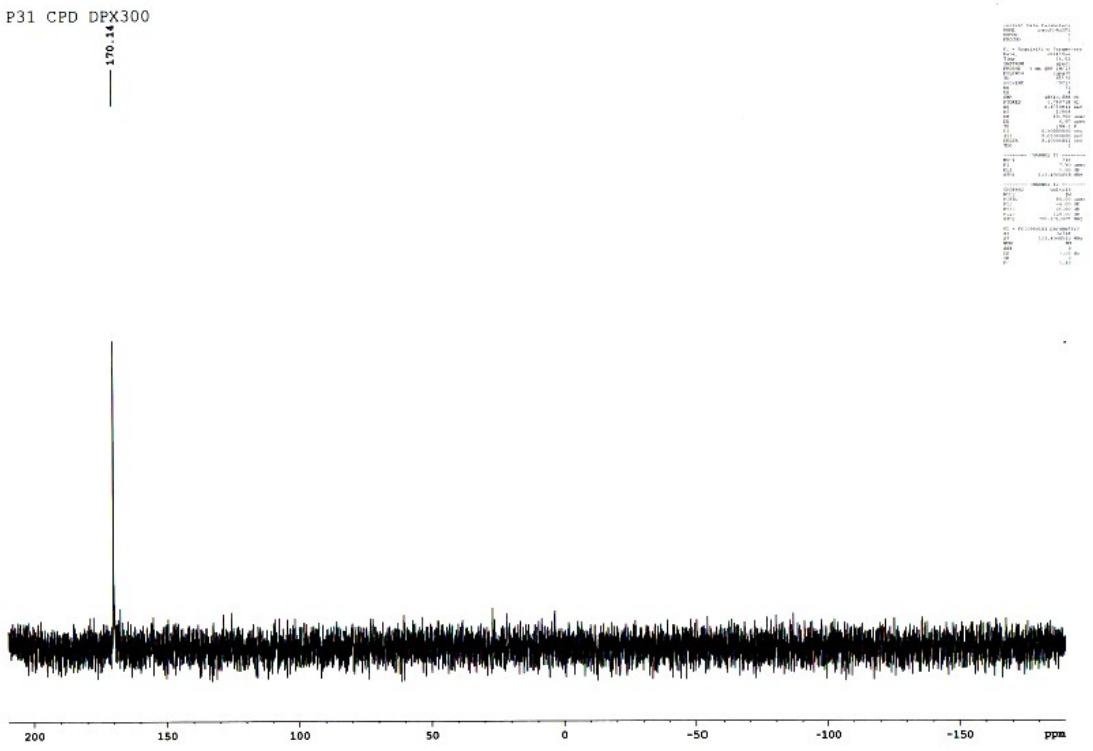
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **2i**



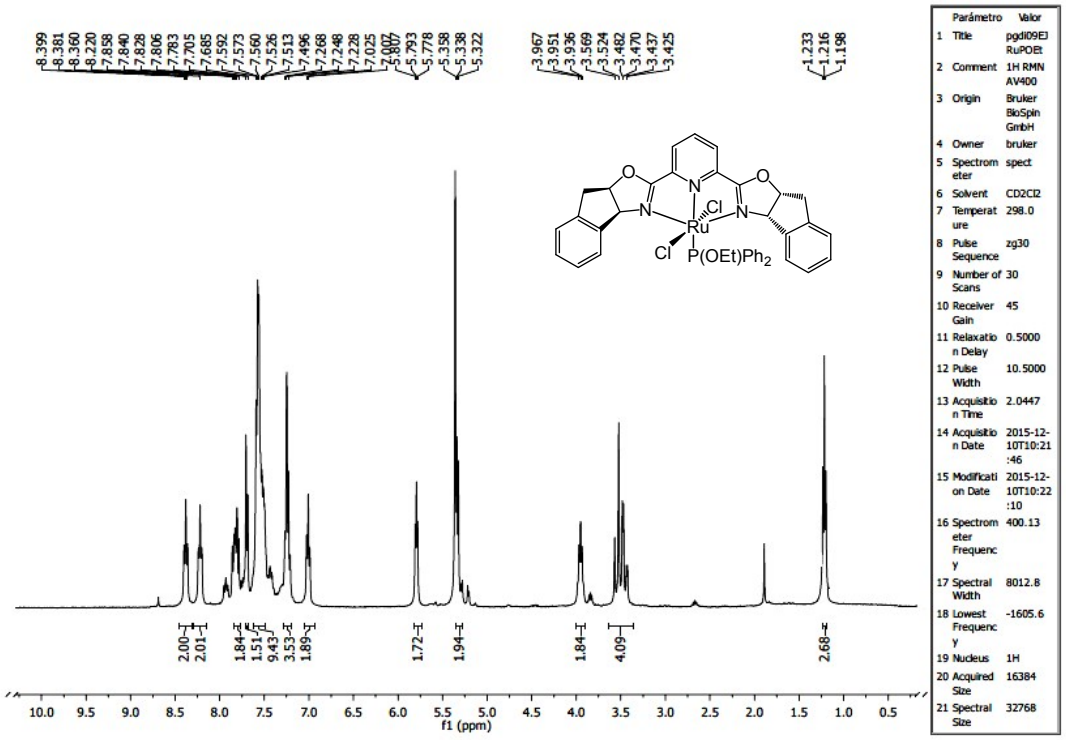
^{1}H NMR (400 MHz, CD_2Cl_2) of **2j**



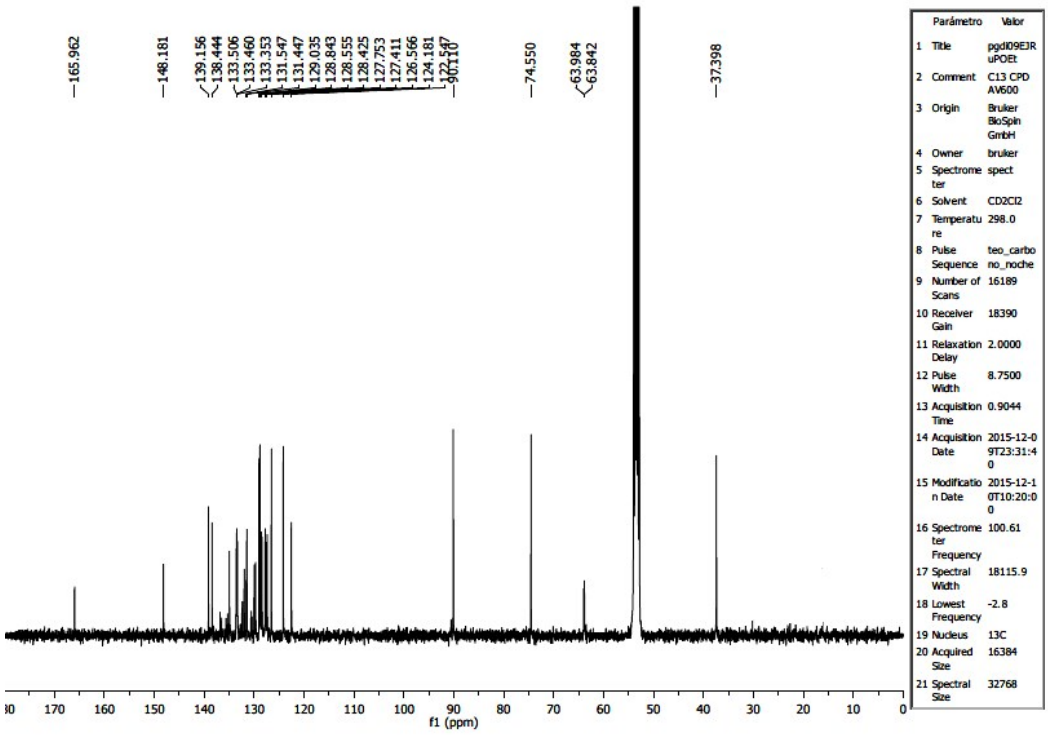
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of **2j**



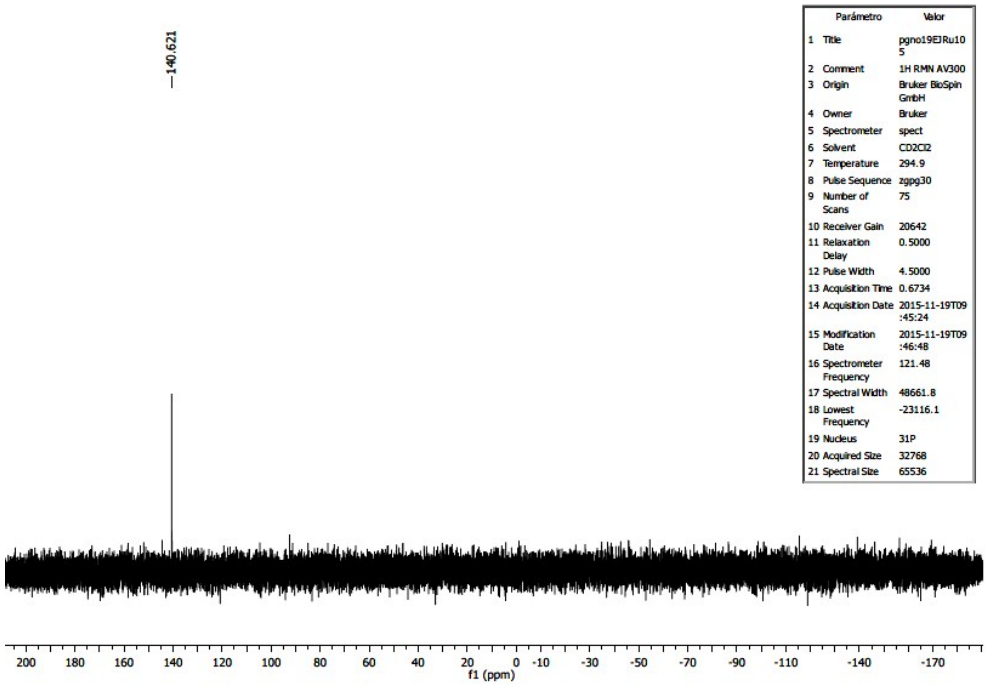
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **2j**



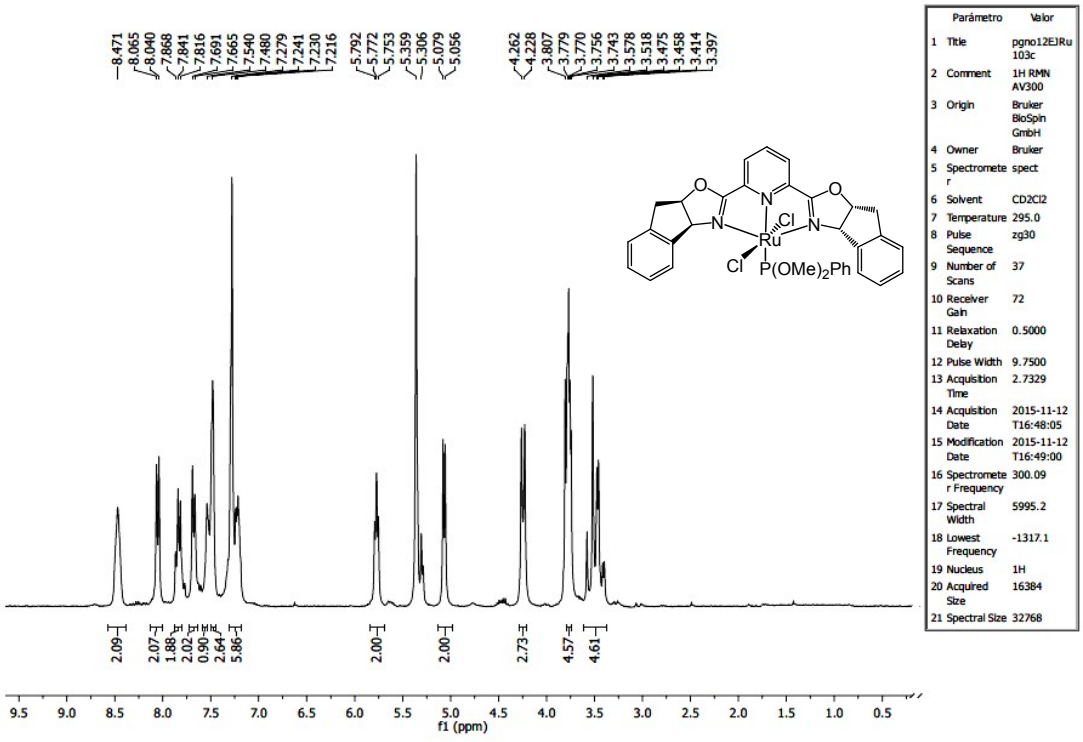
^{1}H NMR (400 MHz, CD_2Cl_2) of **3i**



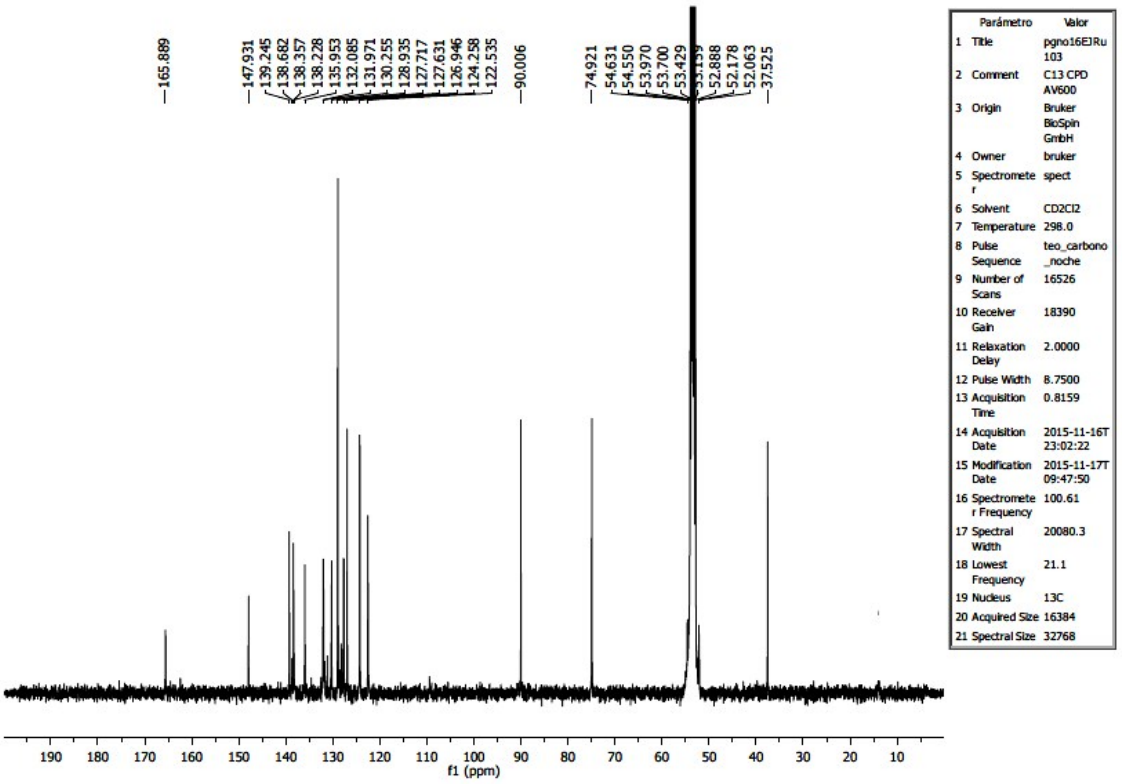
^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2) of **3i**



$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2) of **3i**

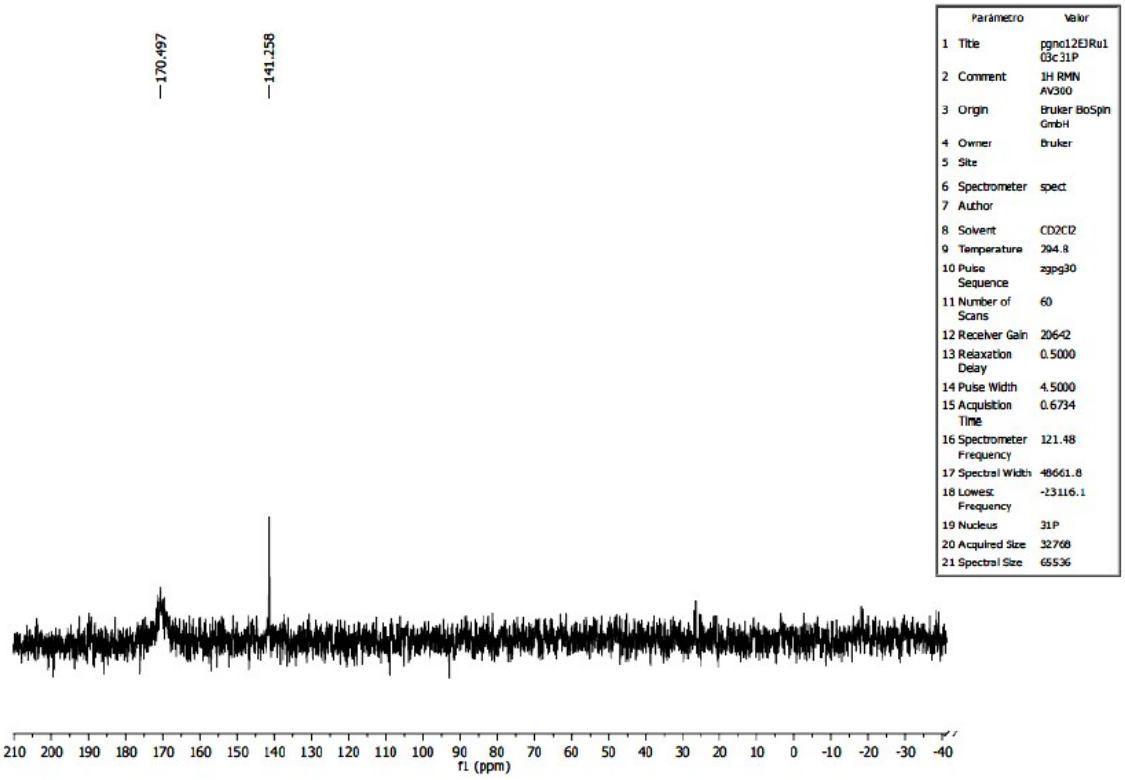


^{1}H NMR (300 MHz, CD_2Cl_2) of **3j**



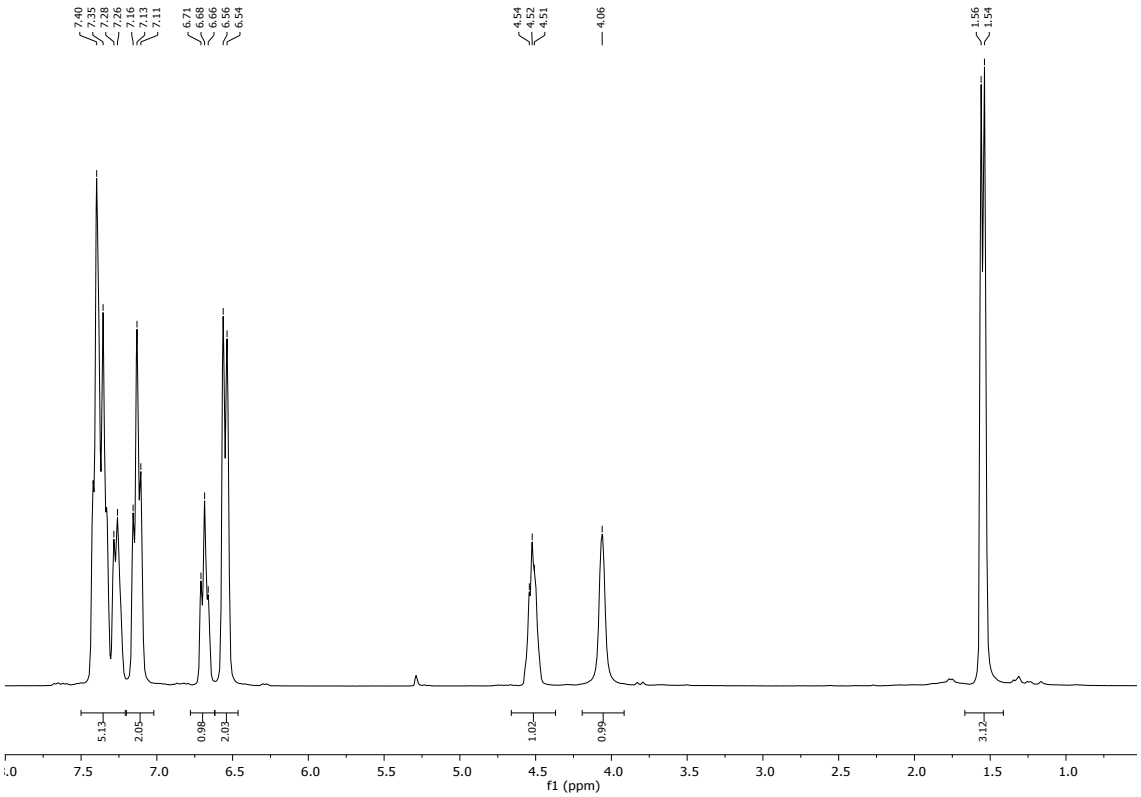
	Parámetro	Valor
1	Title	pgno16EJRu103
2	Comment	C13 CPD AV600
3	Origin	Bruker BioSpin GmbH
4	Owner	bruker
5	Spectrometer	spect
6	Solvent	CD2Cl2
7	Temperature	298.0
8	Pulse Sequence	teo_carbono_noche
9	Number of Scans	16526
10	Receiver Gain	18390
11	Relaxation Delay	2.0000
12	Pulse Width	8.7500
13	Acquisition Time	0.8159
14	Acquisition Date	2015-11-16T 23:02:22
15	Modification Date	2015-11-17T 09:47:50
16	Spectrometer Frequency	100.61
17	Spectral Width	20080.3
18	Lowest Frequency	21.1
19	Nucleus	13C
20	Acquired Size	16384
21	Spectral Size	32768

$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2) of **3j**

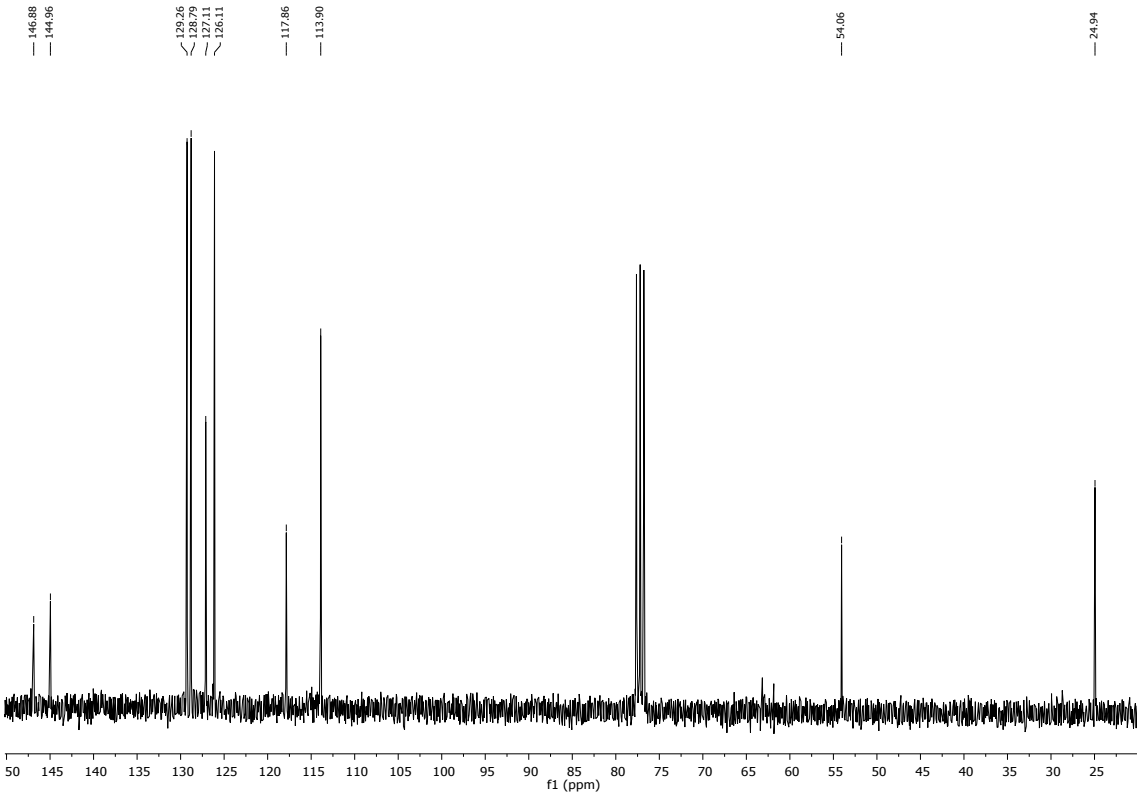


	Parámetro	Valor
1	Title	pgno12EJRu103c31P
2	Comment	1H RMN AV300
3	Origin	Bruker BioSpin GmbH
4	Owner	Bruker
5	Site	
6	Spectrometer	spect
7	Author	
8	Solvent	CD2Cl2
9	Temperature	294.8
10	Pulse Sequence	zgpg30
11	Number of Scans	60
12	Receiver Gain	20642
13	Relaxation Delay	0.5000
14	Pulse Width	4.5000
15	Acquisition Time	0.6734
16	Spectrometer Frequency	121.48
17	Spectral Width	48661.8
18	Lowest Frequency	-23116.1
19	Nucleus	31P
20	Acquired Size	32768
21	Spectral Size	65536

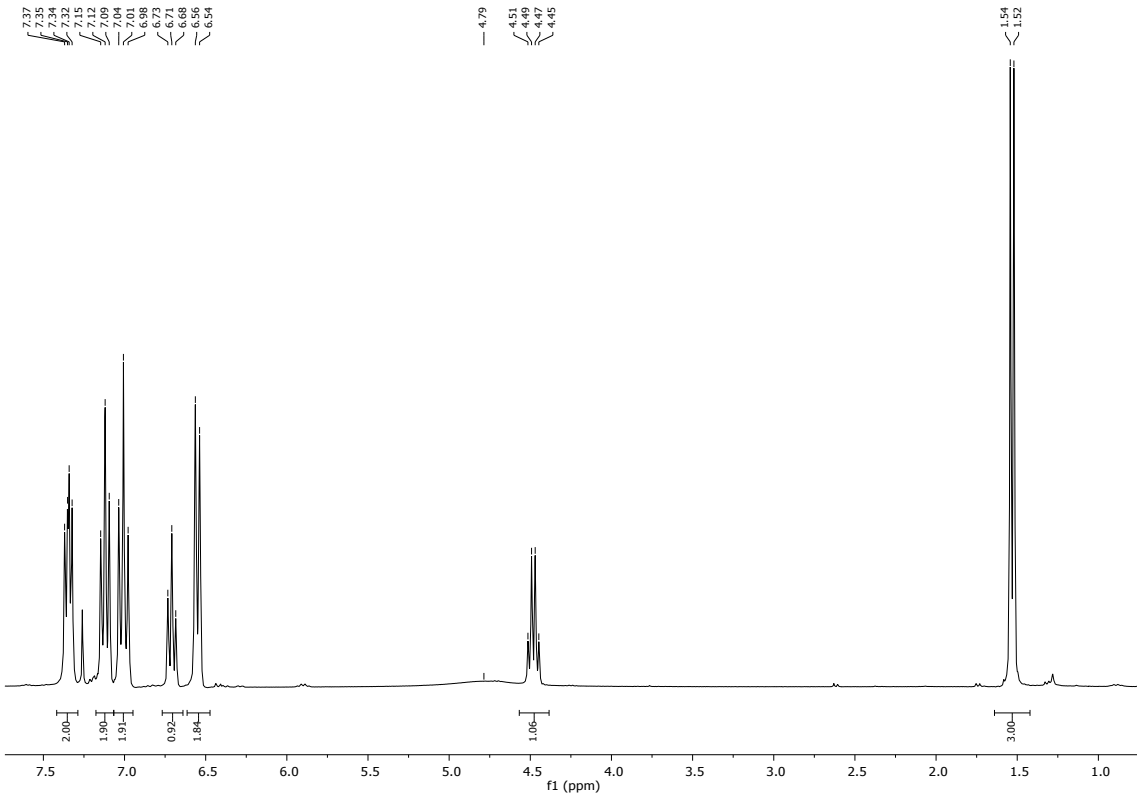
$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2) of **3j**



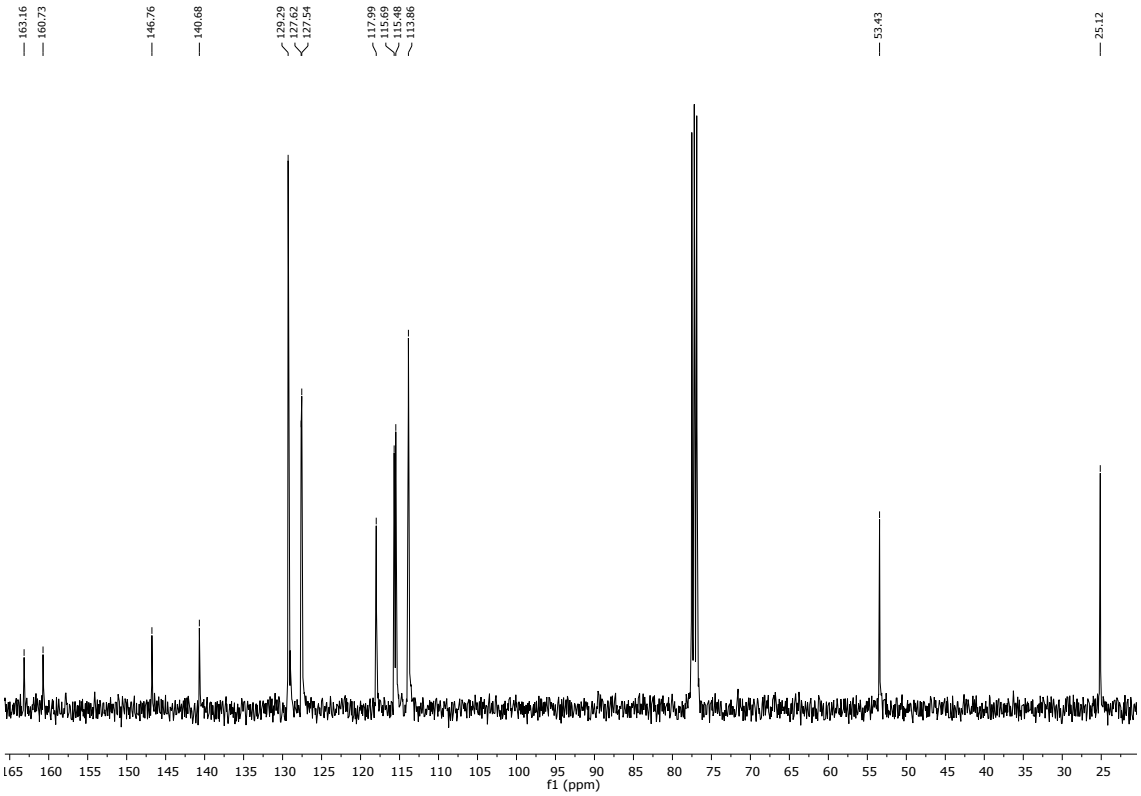
^{1}H NMR (300 MHz, $CDCl_3$) of *(S)-N*-phenyl-1-phenylethylamine (**5a**)



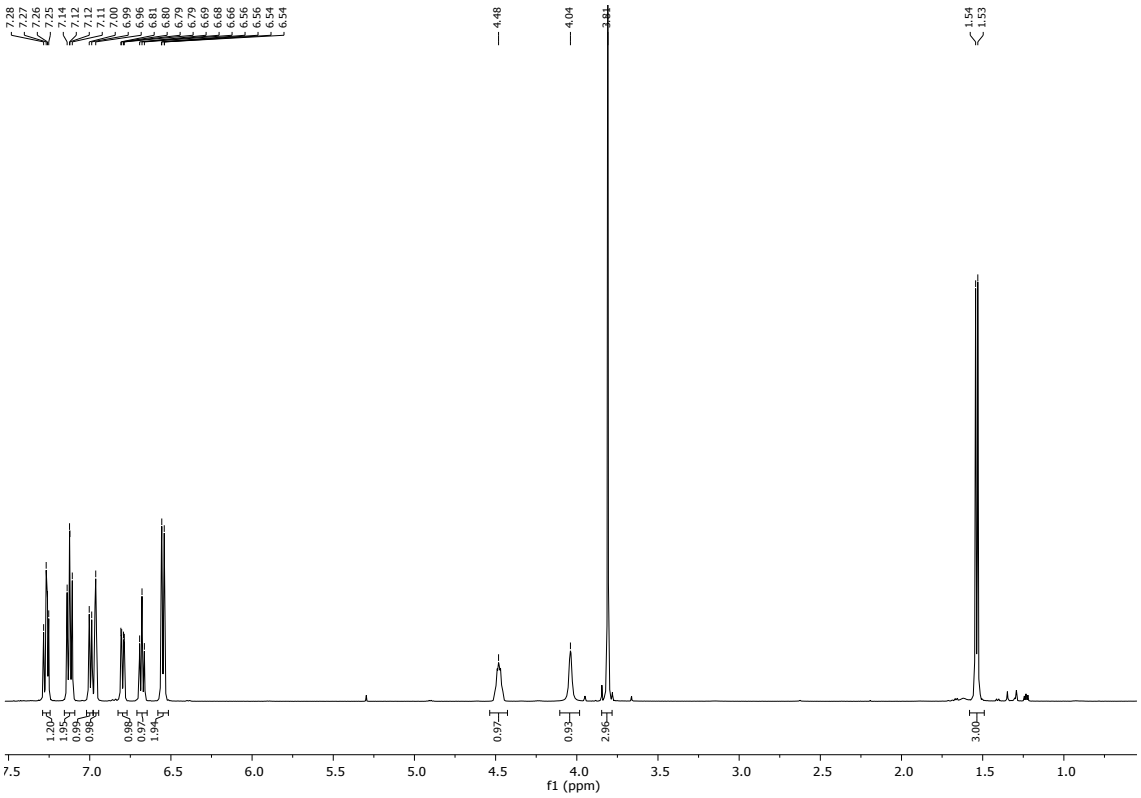
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of *(S)-N*-phenyl-1-phenylethylamine (**5a**)



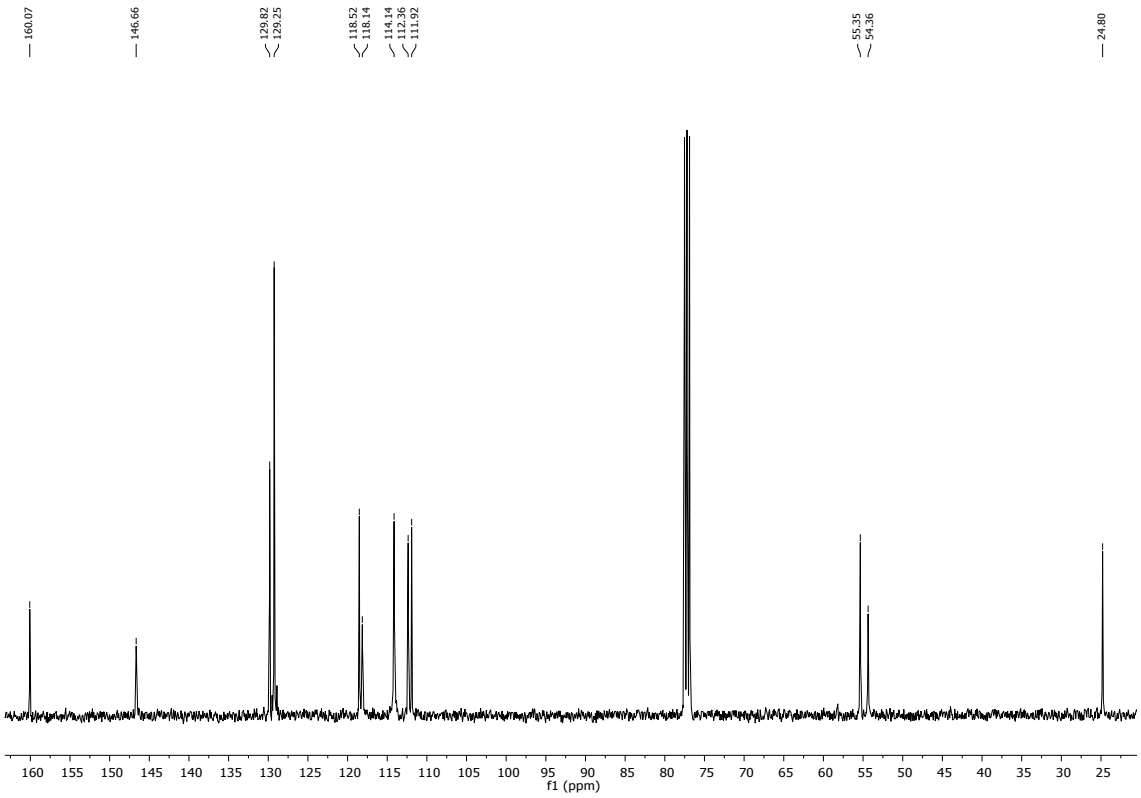
^{1}H NMR (300 MHz, $CDCl_3$) of *(S)*-*N*-phenyl-1-(*p*-fluorophenyl)ethylamine (**5b**)



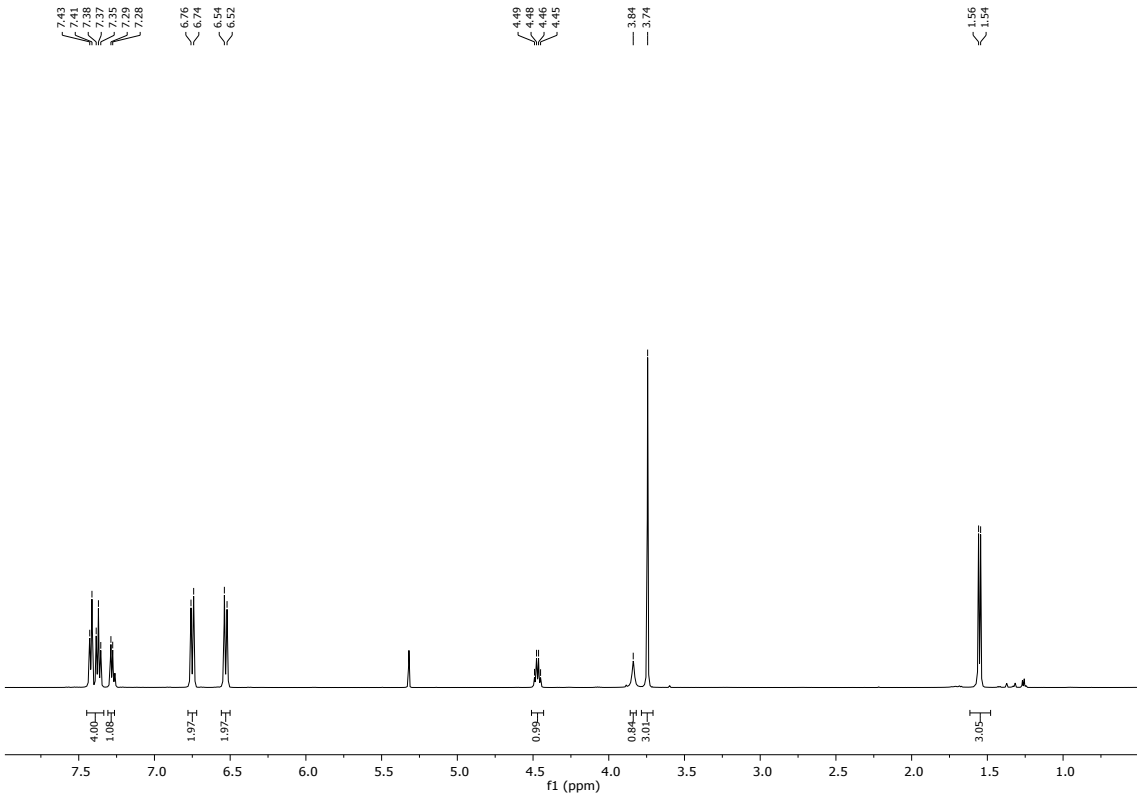
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of *(S)*-*N*-phenyl-1-(*p*-fluorophenyl)ethylamine (**5b**)



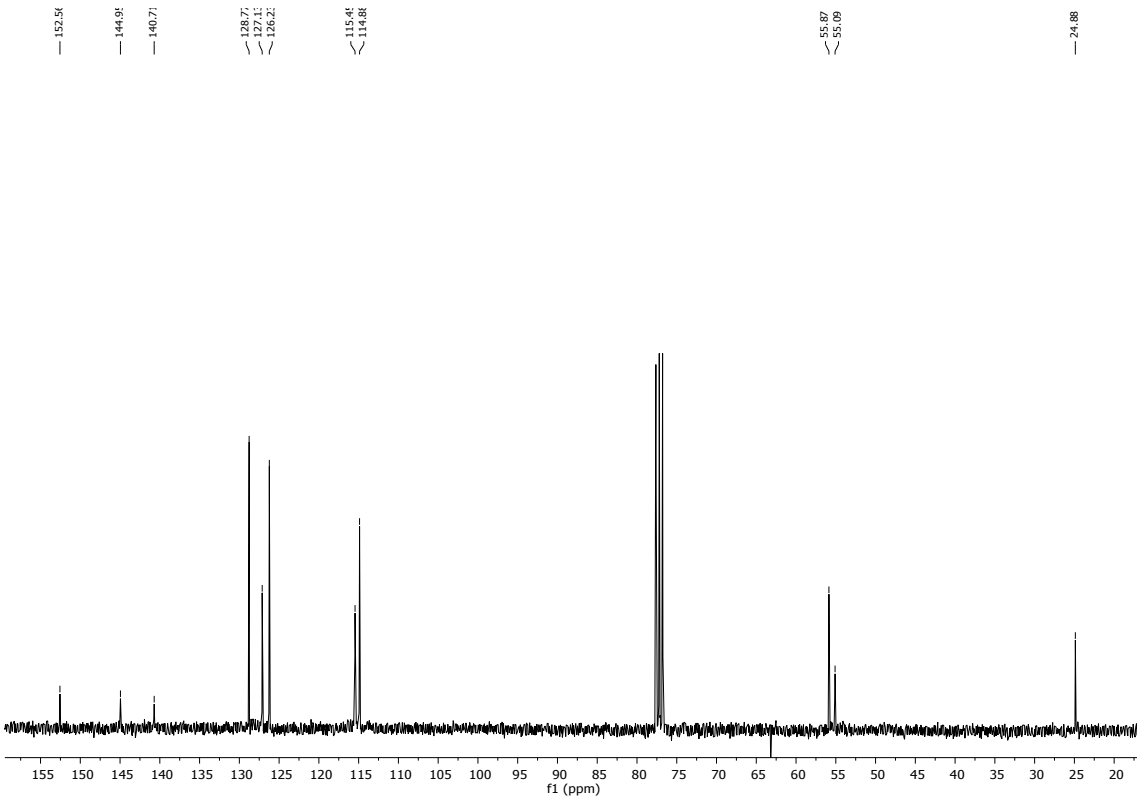
^{1}H NMR (500 MHz, $CDCl_3$) of *(S)*-*N*-phenyl-1-(*m*-methoxyphenyl)ethylamine (**5d**)



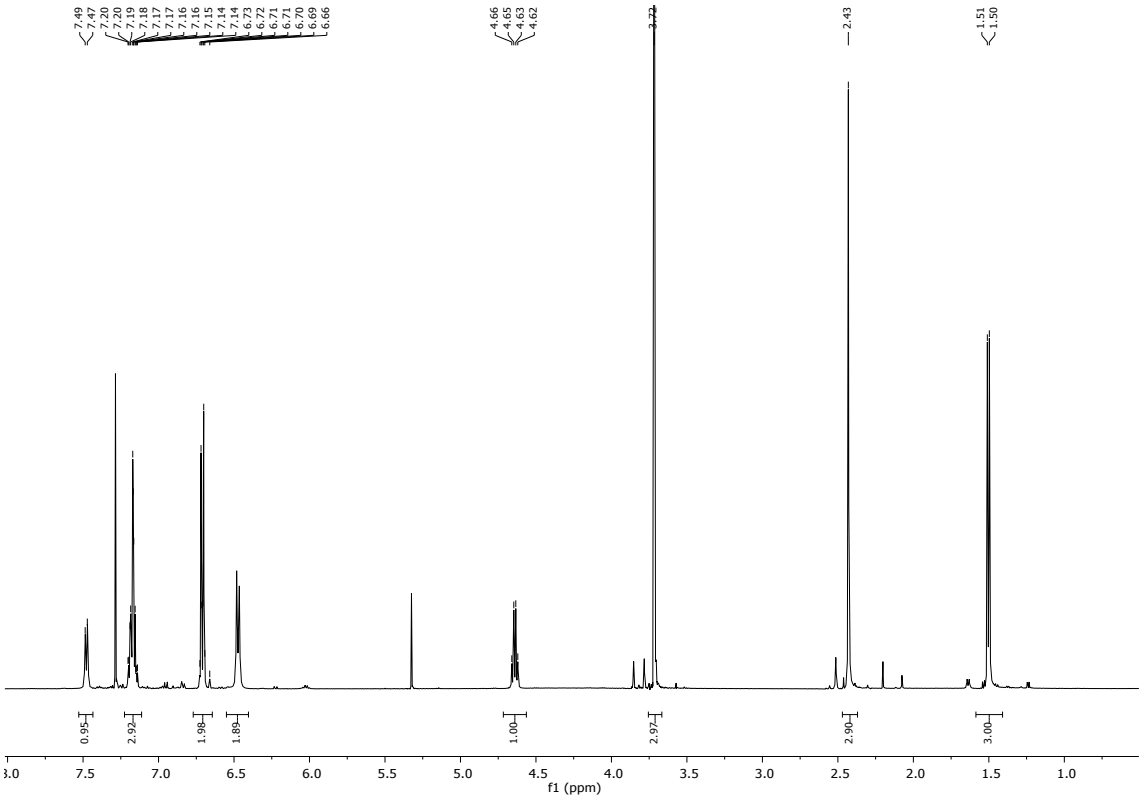
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of *(S)*-*N*-phenyl-1-(*m*-methoxyphenyl)ethylamine (**5d**)



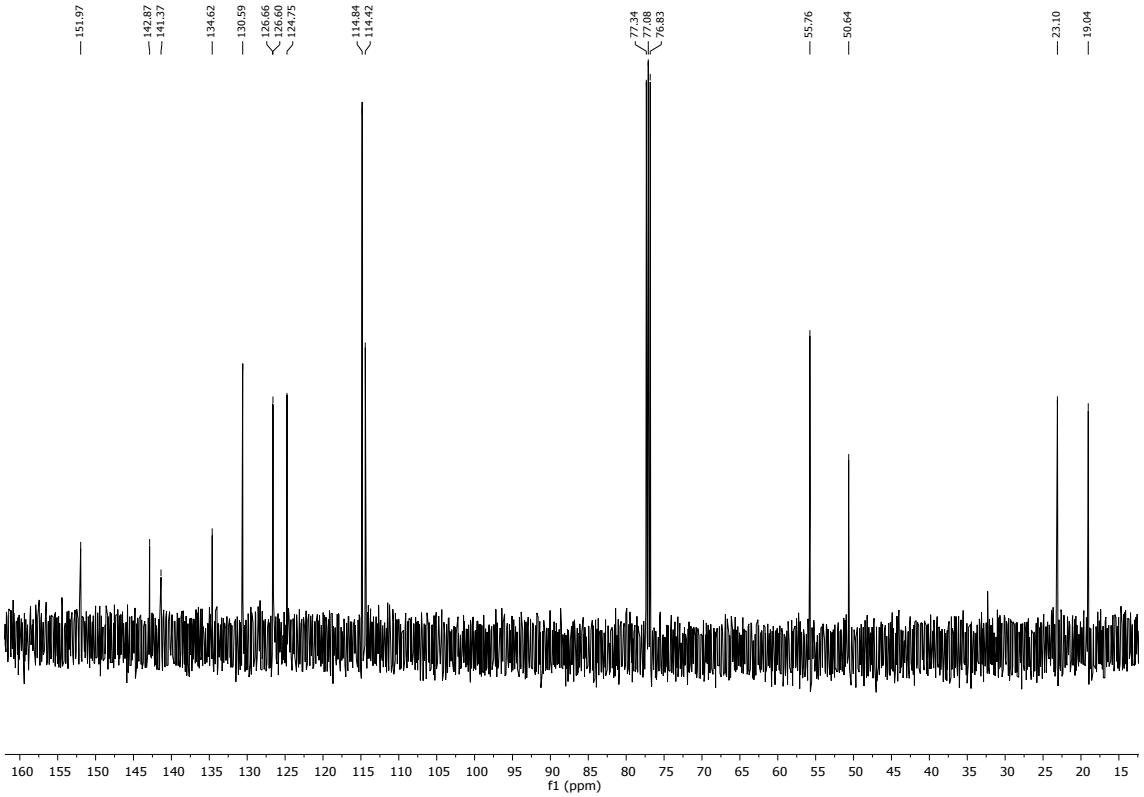
^{1}H NMR (500 MHz, $CDCl_3$) of *(S)-N*-(*p*-methoxyphenyl)-1-phenylethylamine (**5e**)



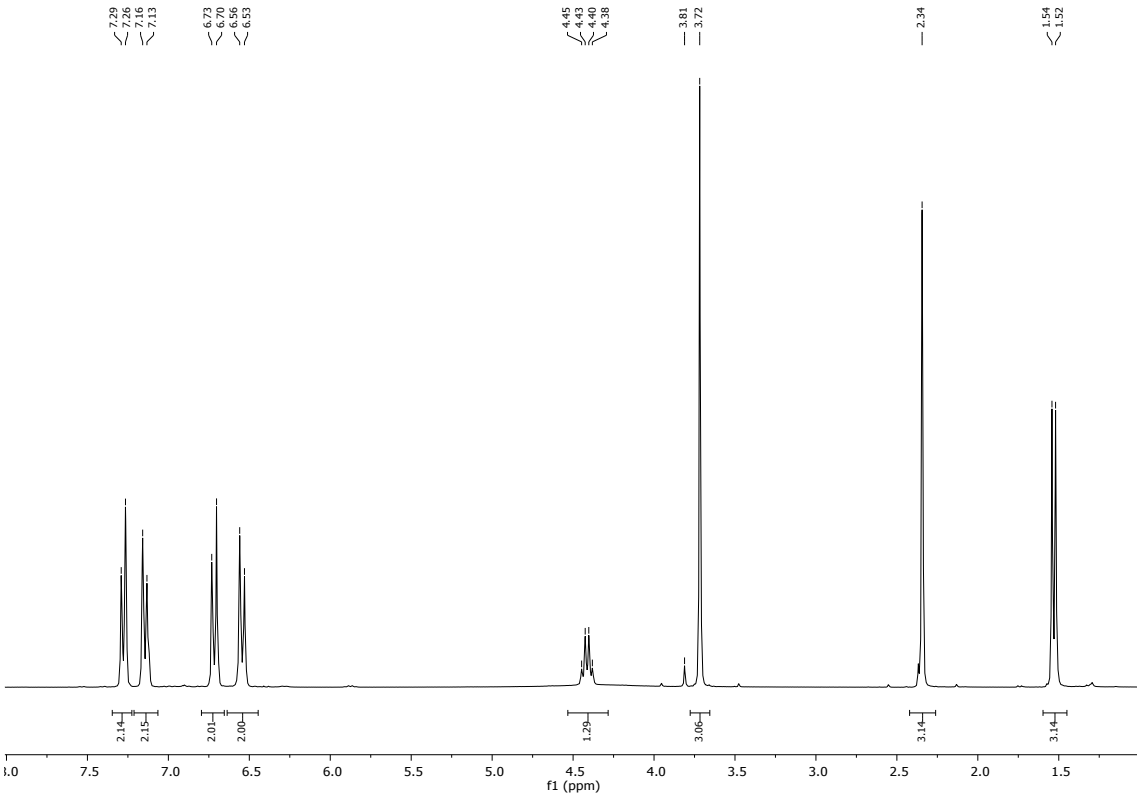
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of *(S)-N*-(*p*-methoxyphenyl)-1-phenylethylamine (**5e**)



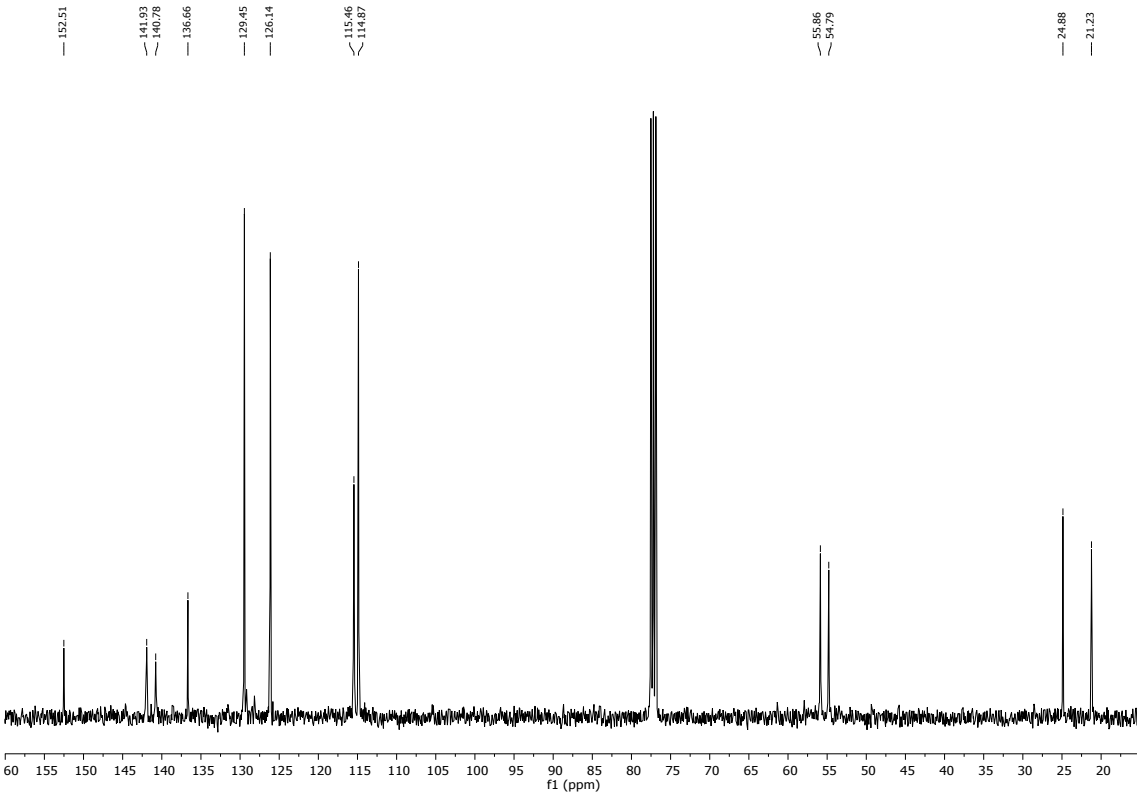
^{1}H NMR (500 MHz, $CDCl_3$) of *N*-(*p*-methoxyphenyl)-1-(*o*-methylphenyl)ethylamine (**5h**)



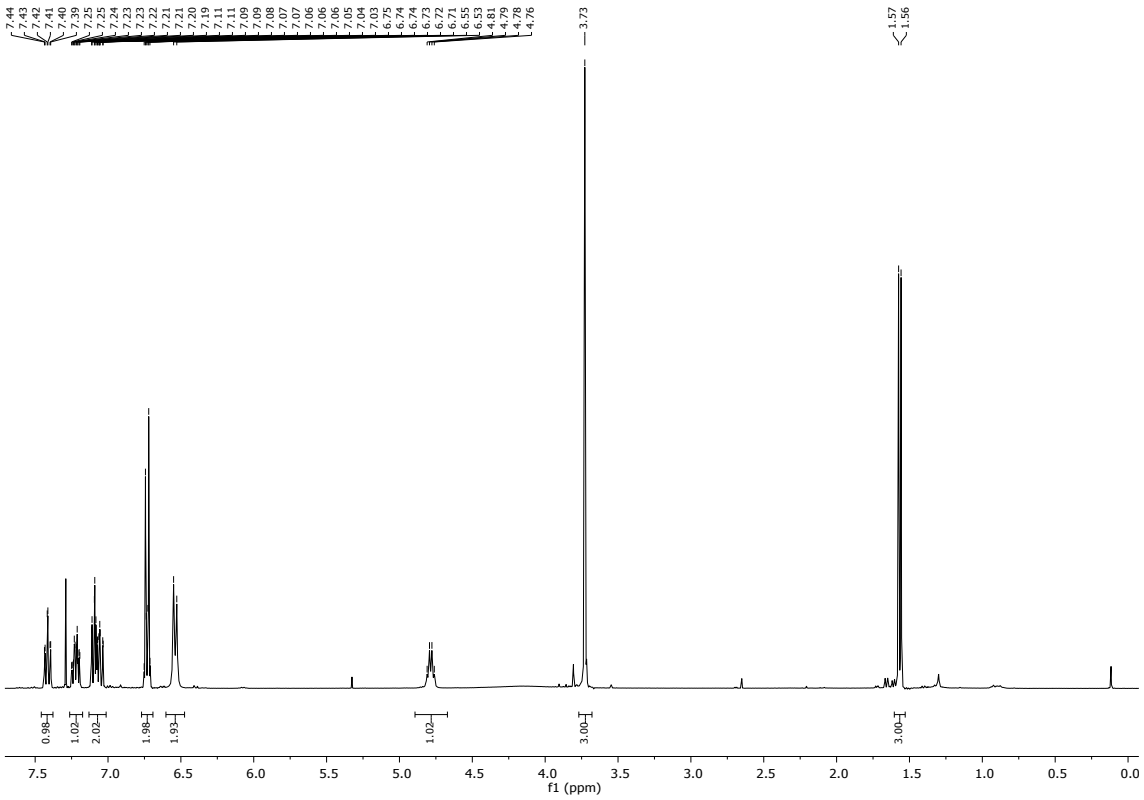
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) of *N*-(*p*-methoxyphenyl)-1-(*o*-methylphenyl)ethylamine (**5h**)



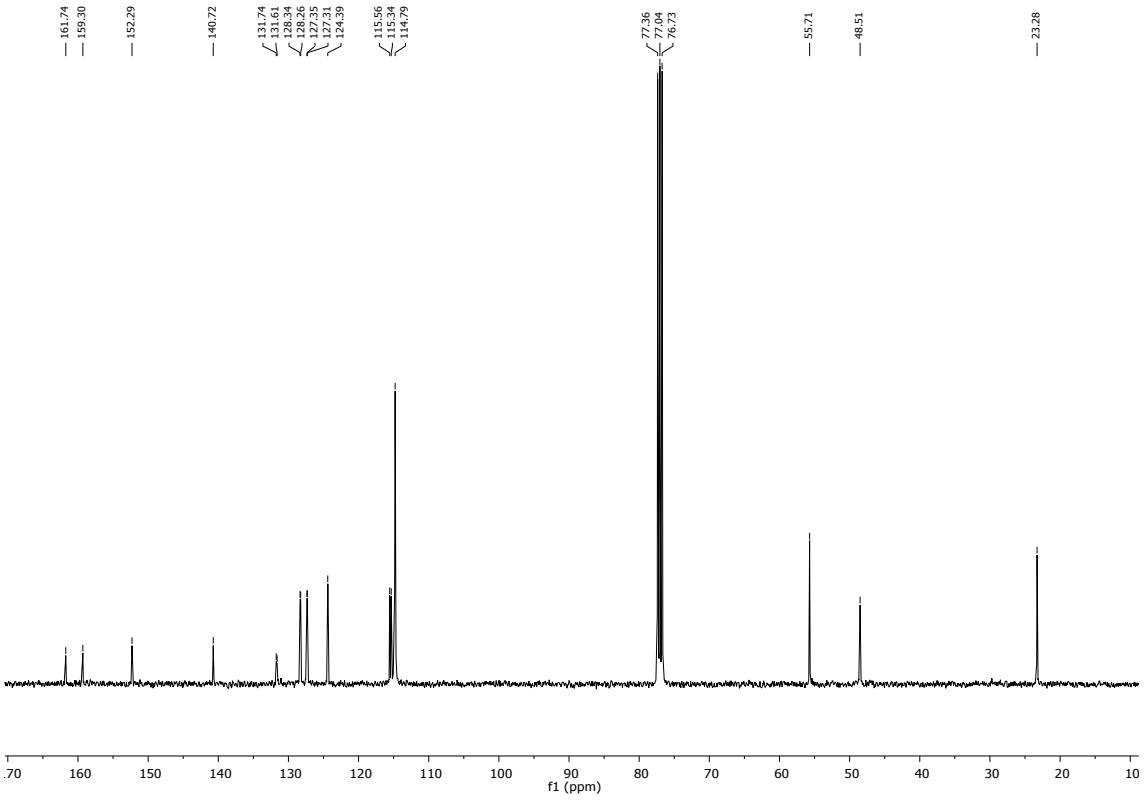
^{1}H NMR (300 MHz, $CDCl_3$) of *(S)-N*-(*p*-Methoxyphenyl)-1-(*p*-methylphenyl)-ethylamine (**5i**)



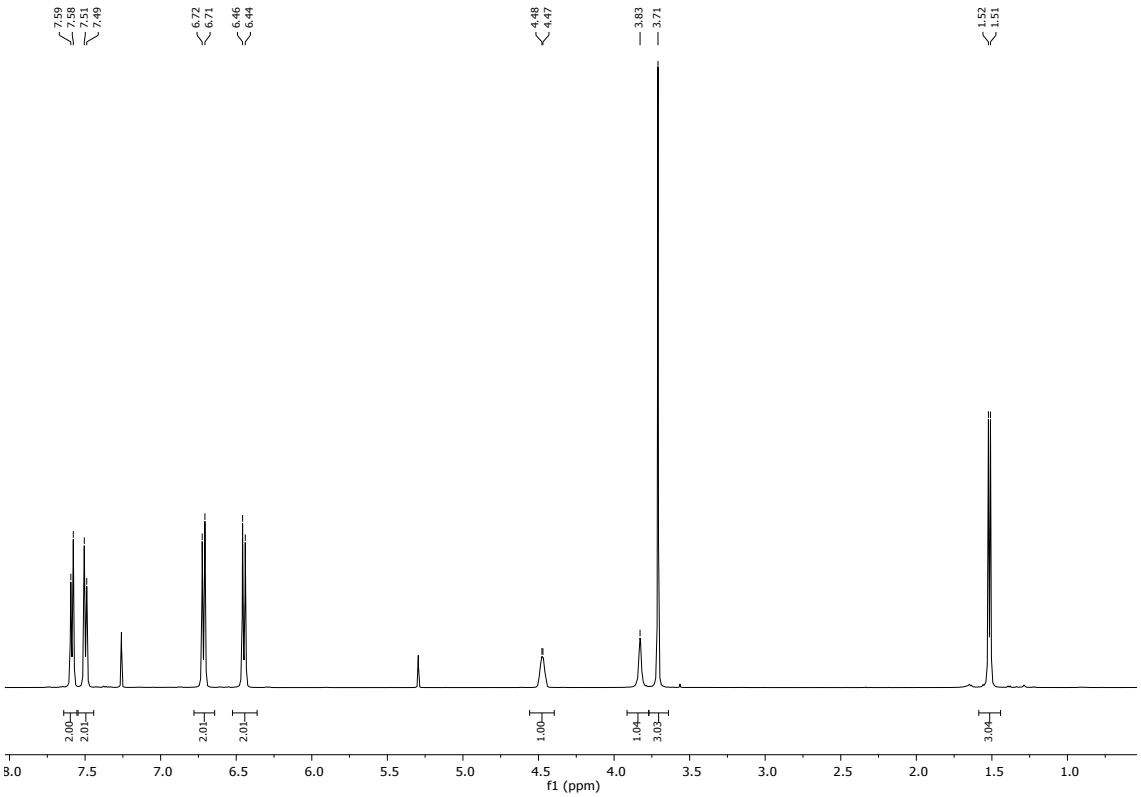
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of *(S)-N*-(*p*-Methoxyphenyl)-1-(*p*-methylphenyl)-ethylamine (**5i**)



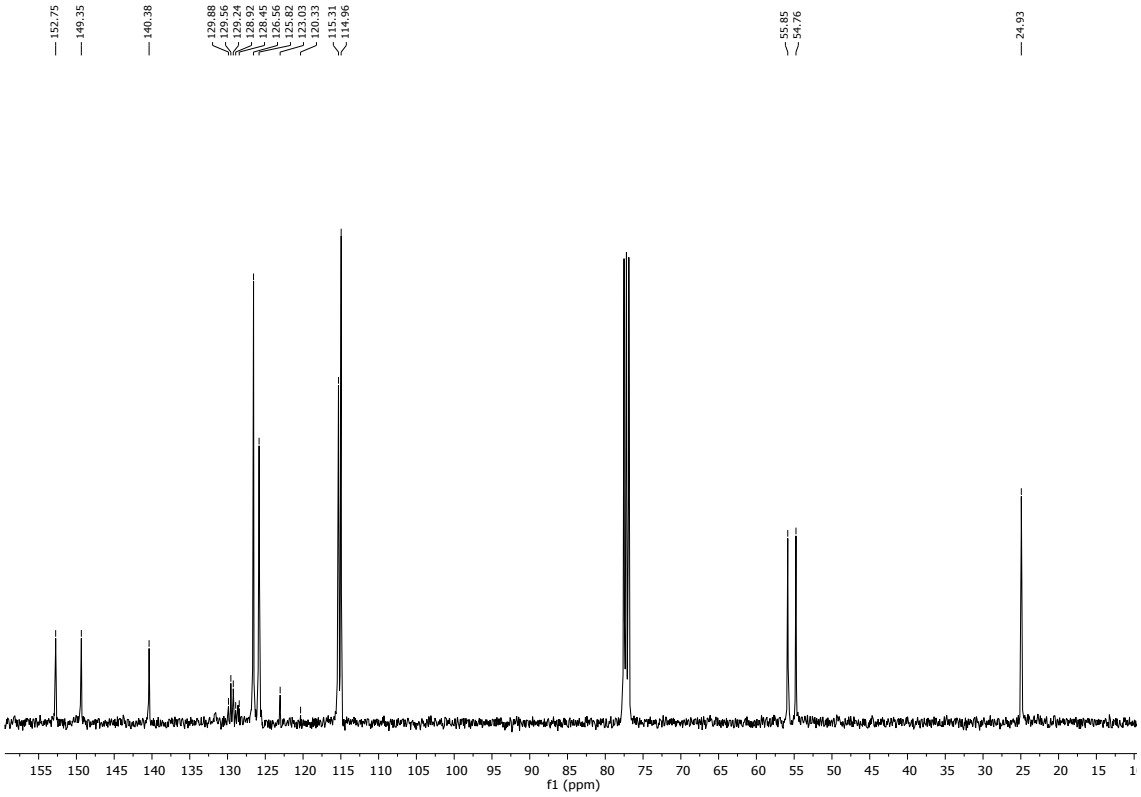
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-(*p*-methoxyphenyl)-1-(*o*-fluorophenyl)ethylamine (**5j**)



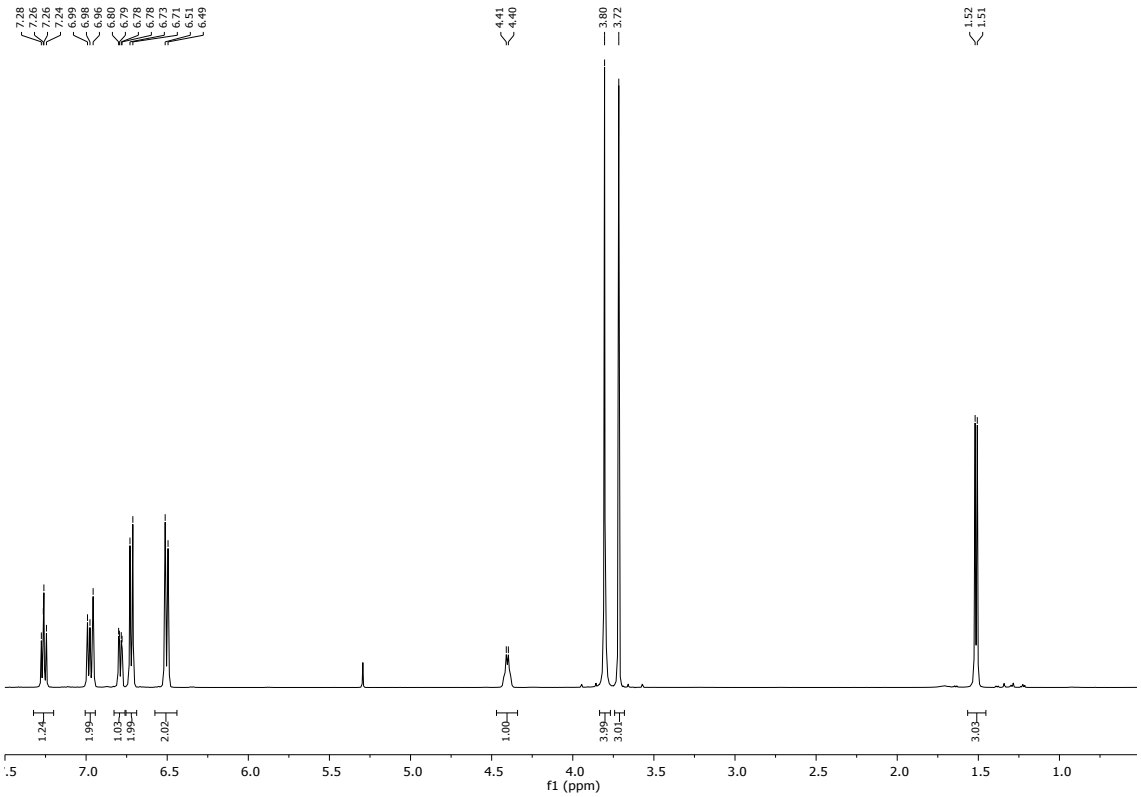
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) of *N*-(*p*-methoxyphenyl)-1-(*o*-fluorophenyl)ethylamine (**5j**)



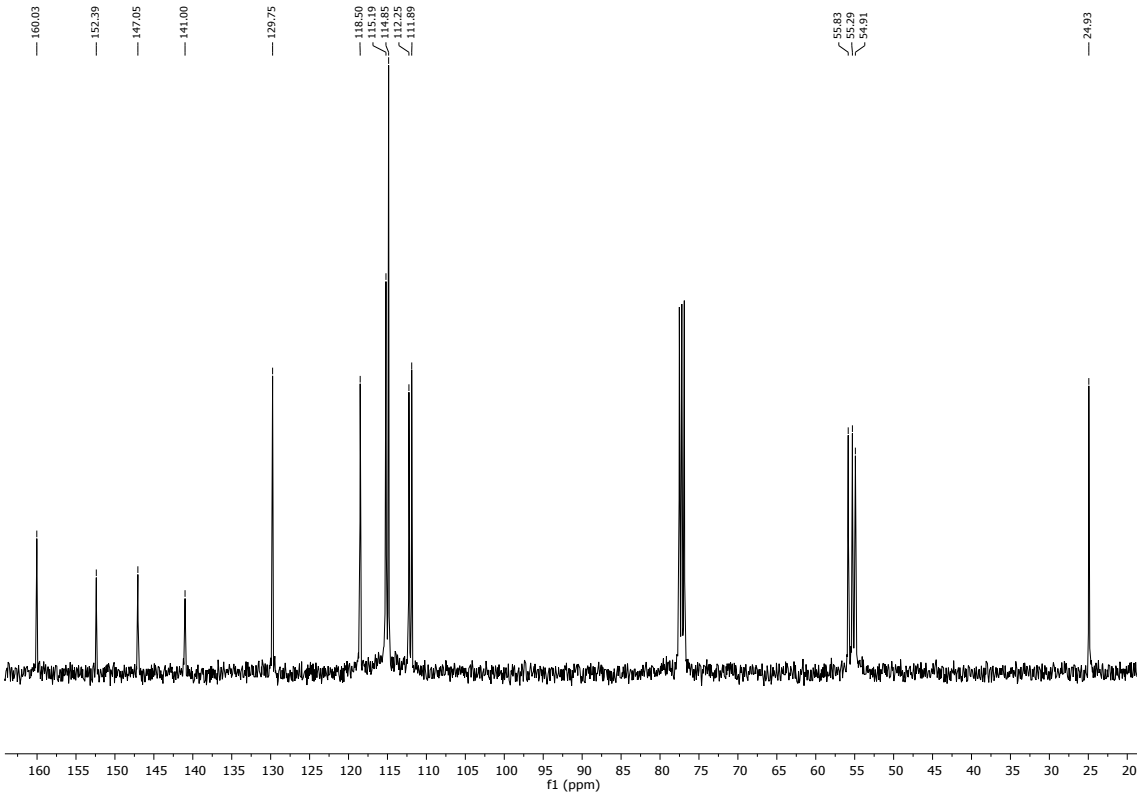
^{1}H NMR (500 MHz, $CDCl_3$) of *(S)-N*-(*p*-Methoxyphenyl)-1-(*p*-trifluoromethylphenyl)-ethylamine (**5k**)



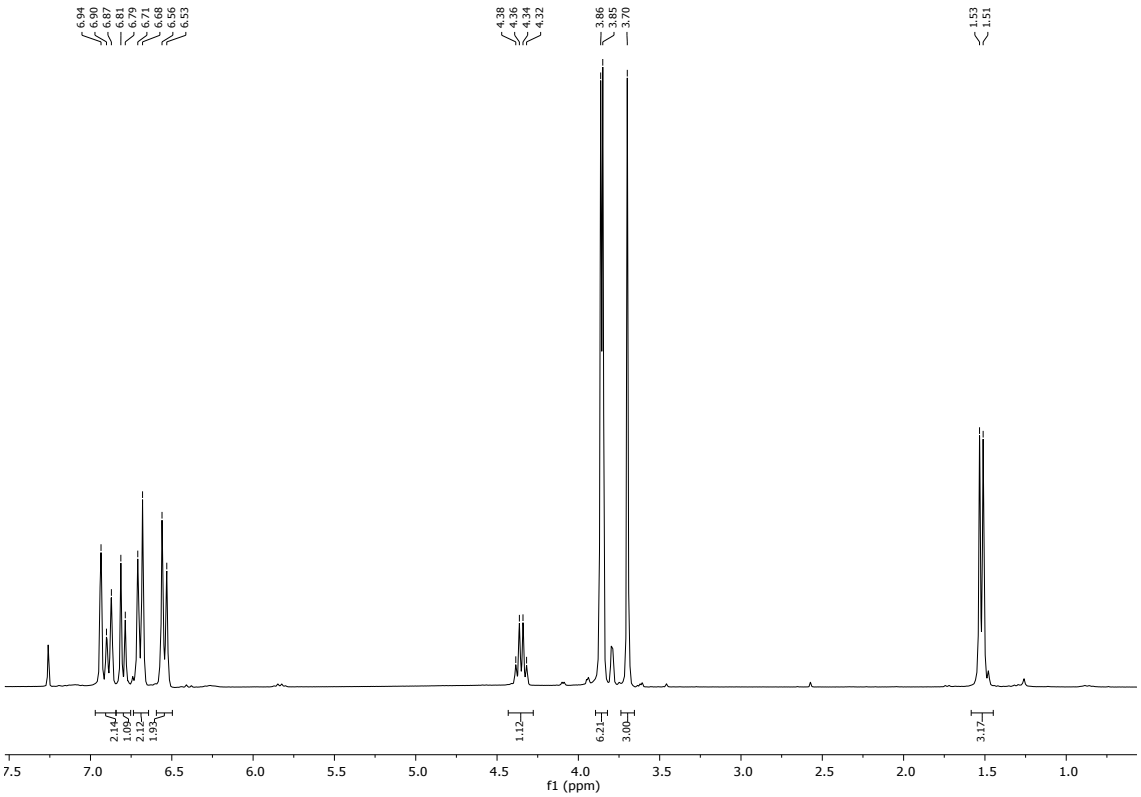
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of *(S)-N*-(*p*-Methoxyphenyl)-1-(*p*-trifluoromethylphenyl)-ethylamine (**5k**)



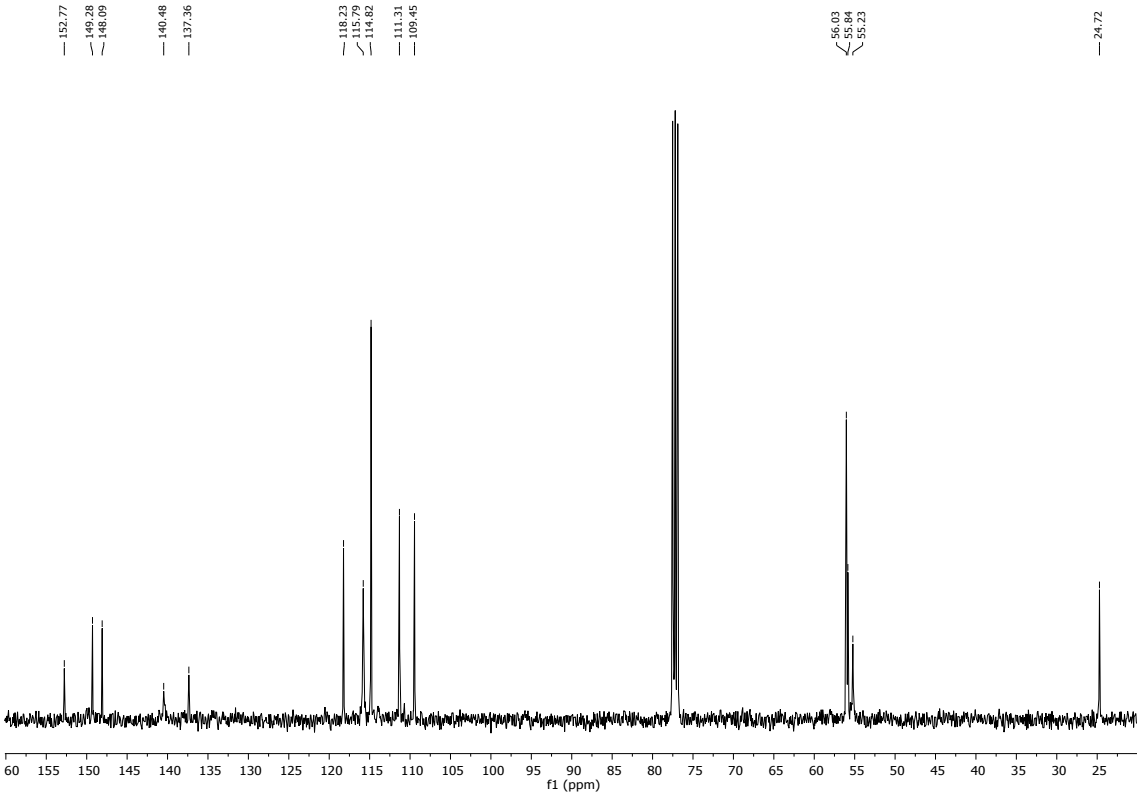
^{1}H NMR (500 MHz, $CDCl_3$) of *(S)*-*N*-(*p*-methoxyphenyl)-1-(*m*-methoxyphenyl)ethylamine (**5l**)



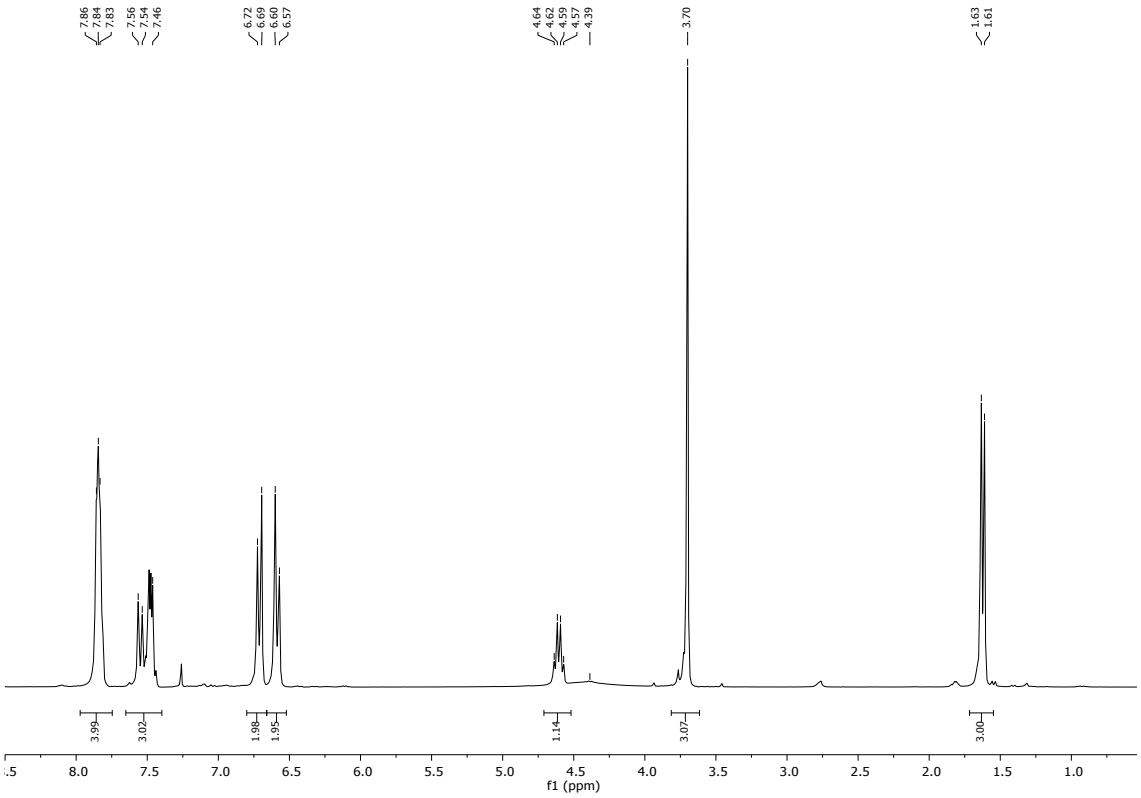
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of *(S)*-*N*-(*p*-methoxyphenyl)-1-(*m*-methoxyphenyl)-ethylamine (**5l**)



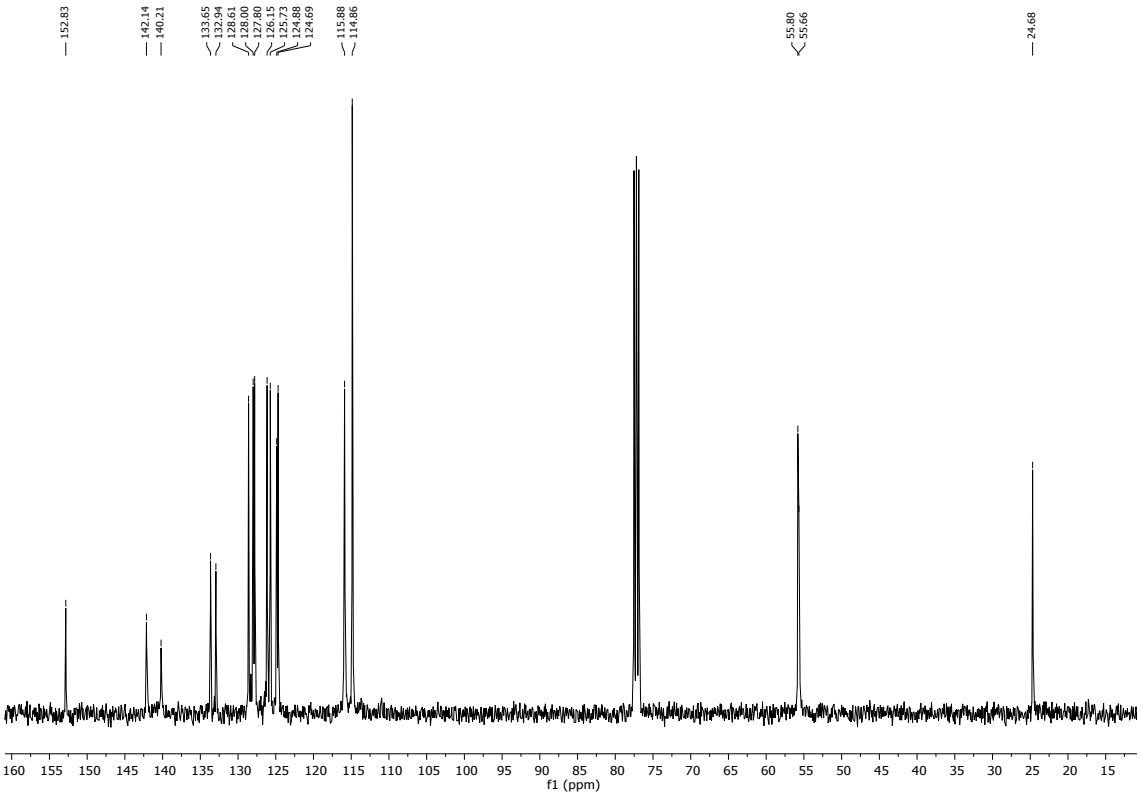
^{1}H NMR (300 MHz, $CDCl_3$) of *(S)-N*-(*p*-methoxyphenyl)-1-(*m,p*-dimethoxyphenyl)-ethylamine (**5m**)



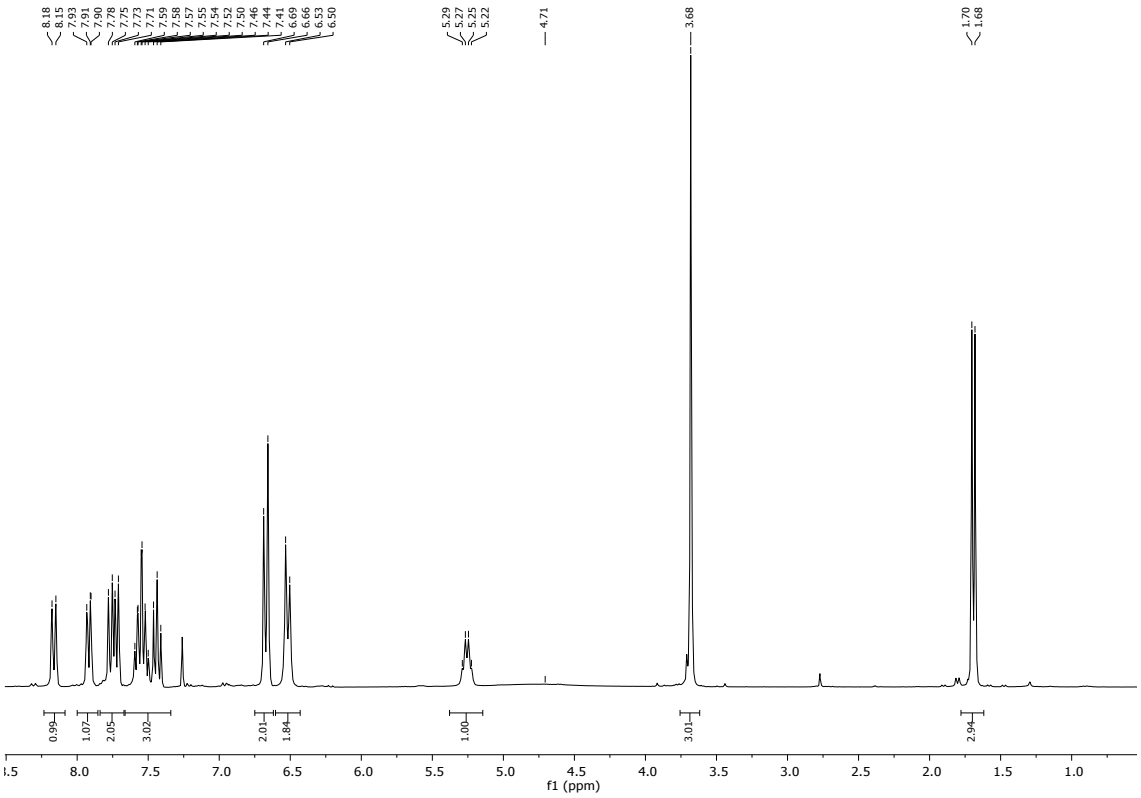
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of *(S)-N*-(*p*-methoxyphenyl)-1-(*m,p*-dimethoxyphenyl)-ethylamine (**5m**)



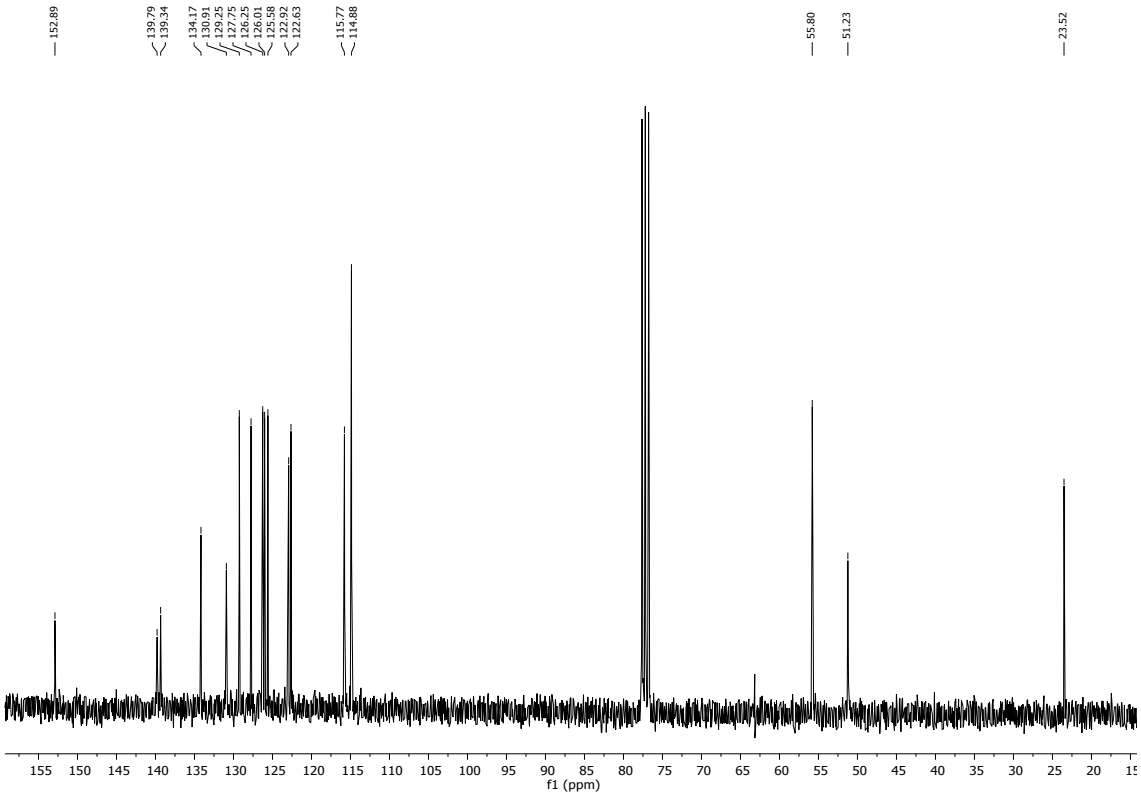
^{1}H NMR (300 MHz, $CDCl_3$) of *(S)-N*-(*p*-methoxyphenyl)-2-naphthylethylamine (**5n**)



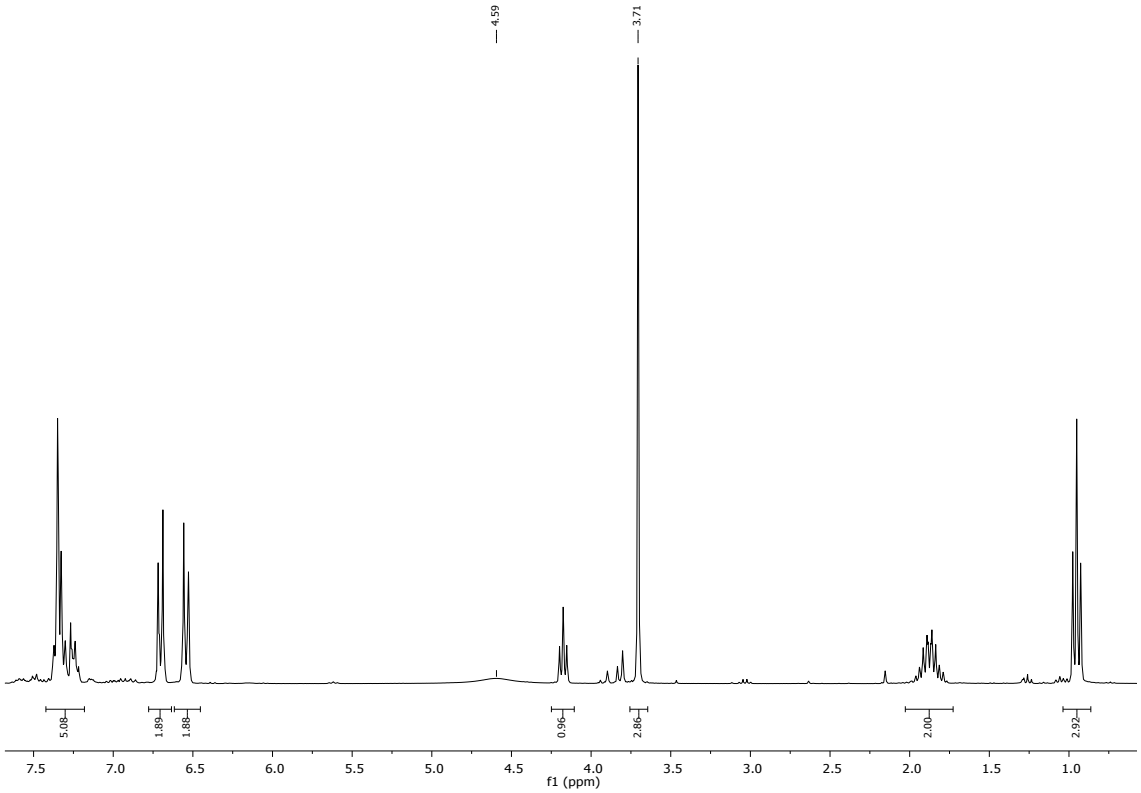
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of *(S)-N*-(*p*-methoxyphenyl)-2-naphthylethylamine (**5n**)



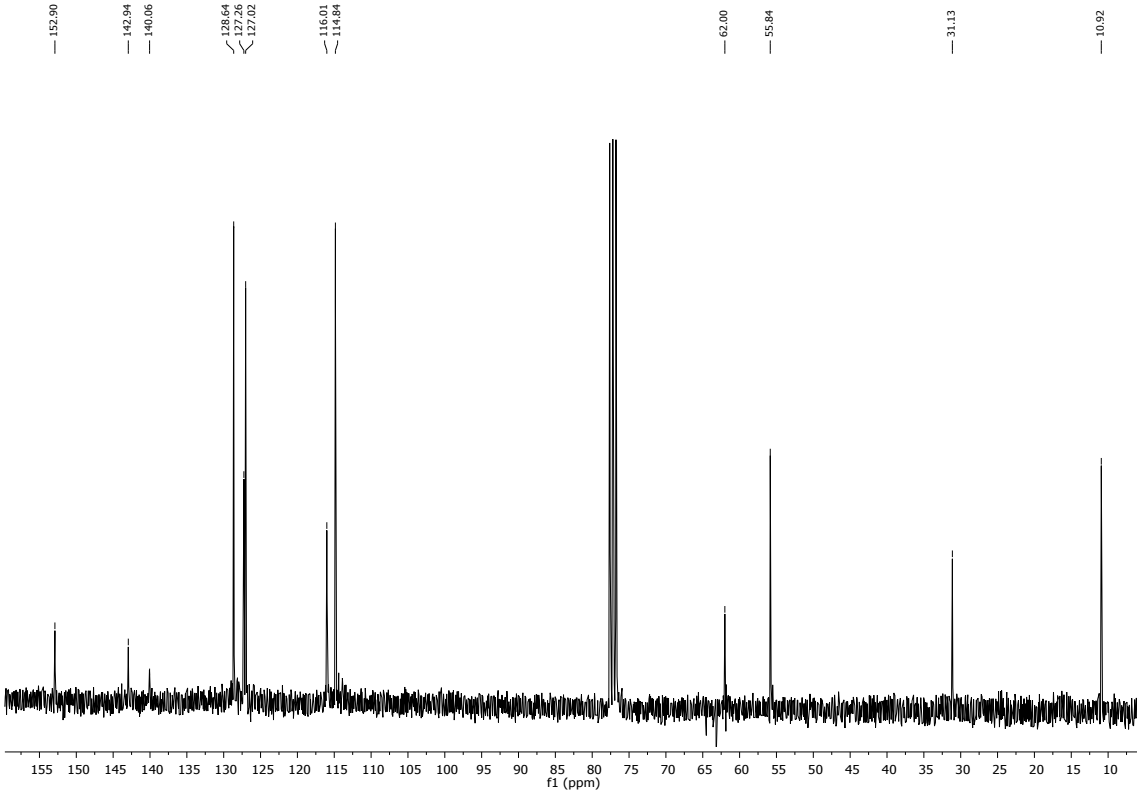
^{1}H NMR (300 MHz, $CDCl_3$) of *(S)-N*-(*p*-methoxyphenyl)-1-naphthylethylamine (**5o**)



$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of *(S)-N*-(*p*-methoxyphenyl)-1-naphthylethylamine (**5o**)

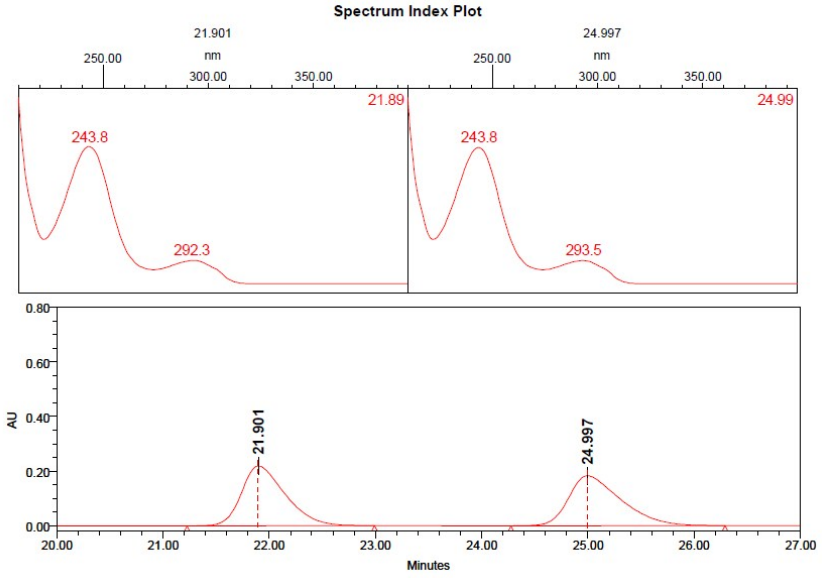


^{1}H NMR (300 MHz, $CDCl_3$) of *(S)-N*-(*p*-methoxyphenyl)-1-phenylpropylamine (**5p**)



^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) of *(S)-N*-(*p*-methoxyphenyl)-1-phenylpropylamine (**5p**)

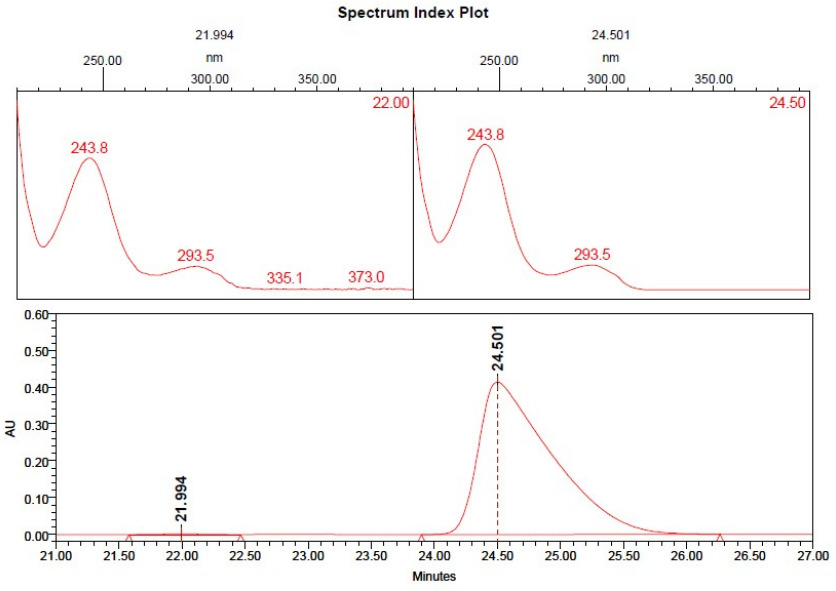
N-phenyl-1-phenylethylamine (5a)



Peak Results

	RT	Area	% Area
1	21.901	6253450	50.00
2	24.997	6253704	50.00

rac-**5a**

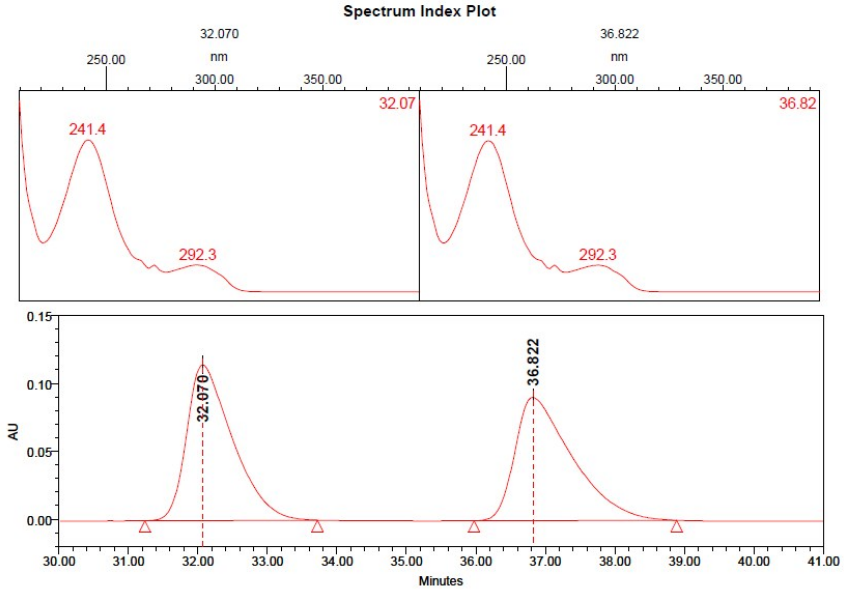


Peak Results

	RT	Area	% Area
1	21.994	45326	0.27
2	24.501	16733488	99.73

(*S*)-**5a**

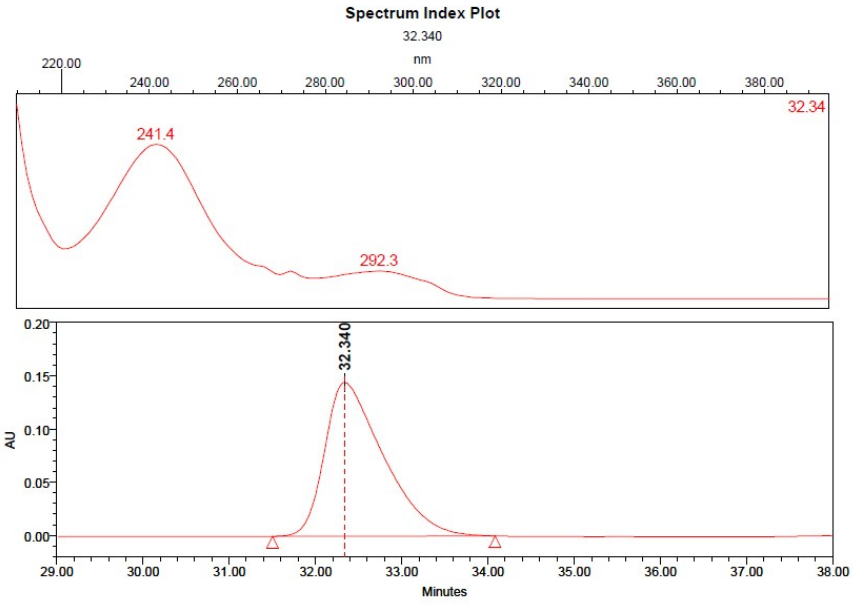
N-phenyl-1-(*p*-fluorophenyl)ethylamine (5b)



Peak Results

	RT	Area	% Area
1	32.070	5264546	50.28
2	36.822	5206863	49.72

rac-**5b**

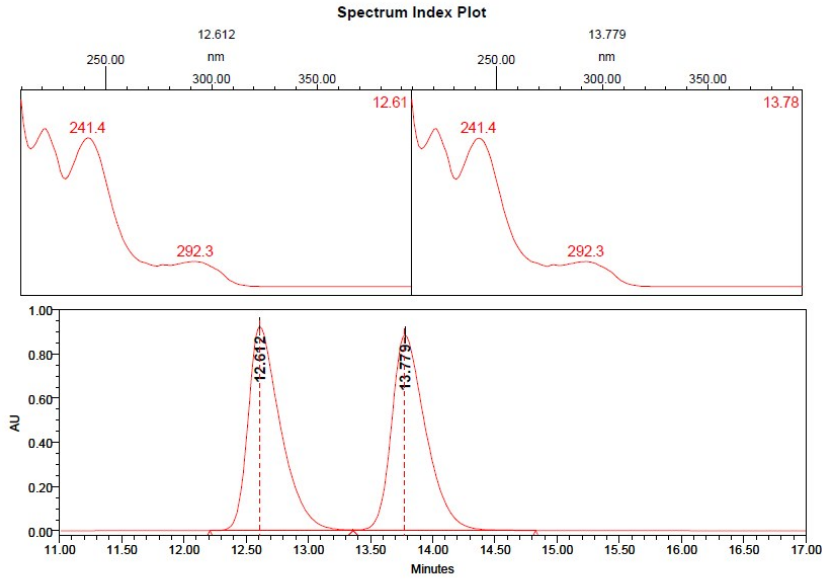


Peak Results

	RT	Area	% Area
1	32.340	6831104	100.00

(*S*)-**5b**

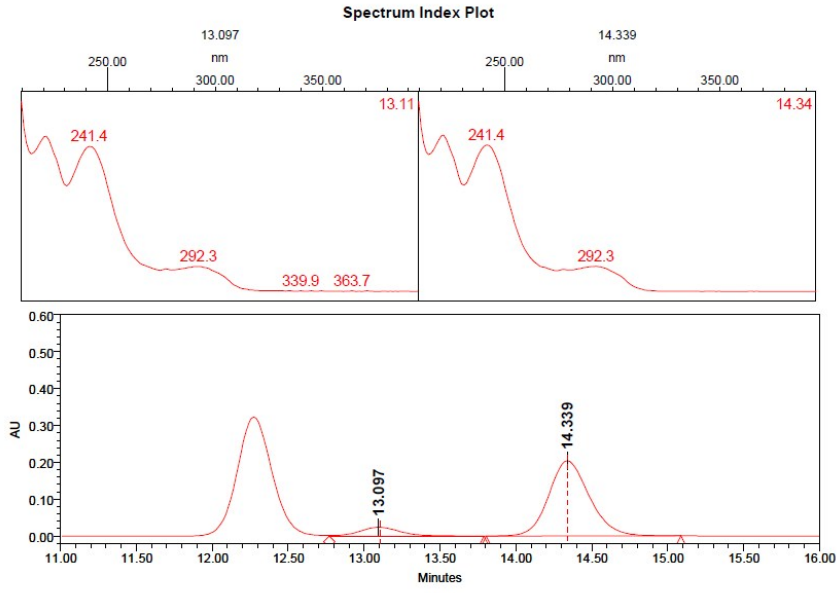
N-phenyl-1-(*p*-chlorophenyl)ethylamine (5c)



Peak Results

	RT	Area	% Area
1	12.612	16748585	49.90
2	13.779	16814780	50.10

rac-**5c**

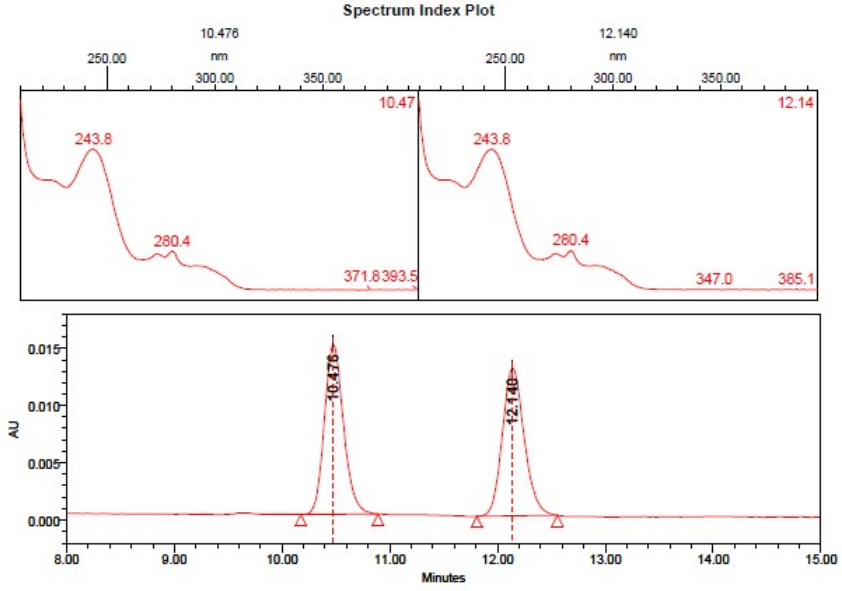


Peak Results

	RT	Area	% Area
1	13.097	440517	10.43
2	14.339	3784799	89.57

5c (79 % ee)

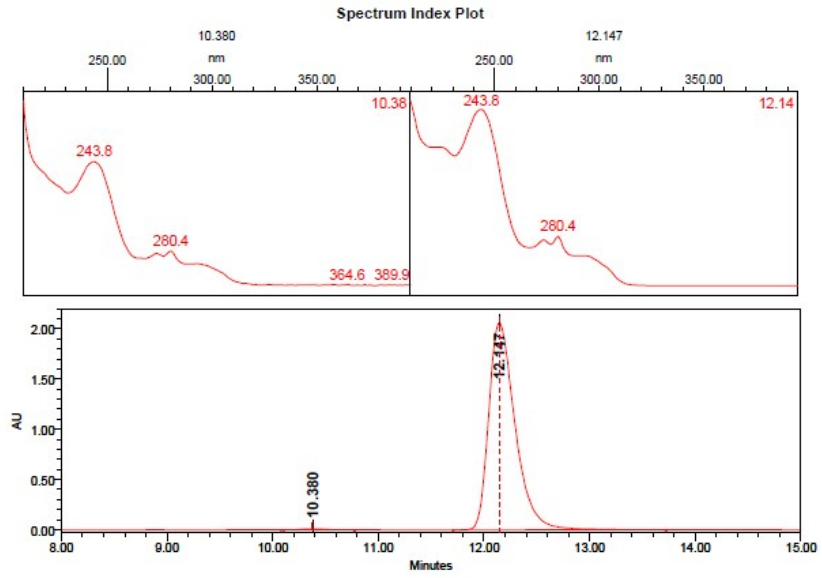
N-phenyl-1-(*m*-methoxyphenyl)ethylamine (5d)



Peak Results

	RT	Area	% Area
1	10.476	182493	50.16
2	12.140	181364	49.84

rac-**5d**

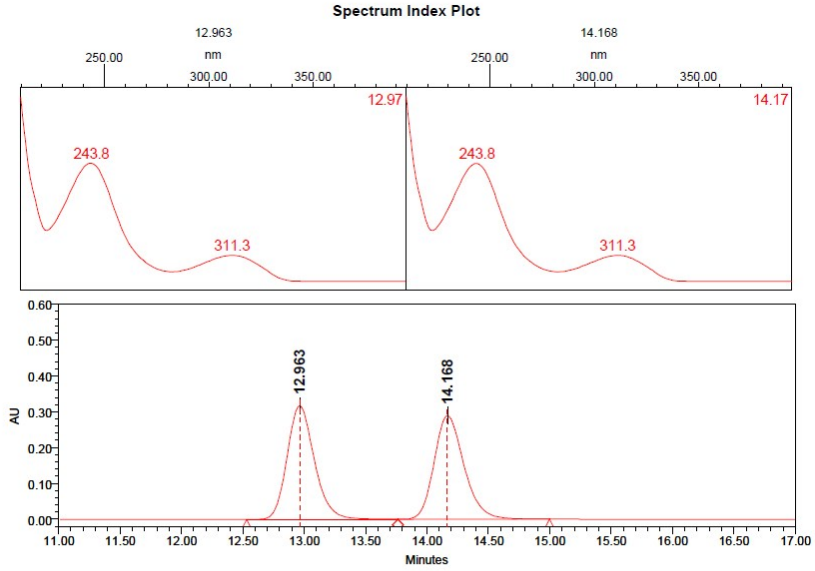


Peak Results

	RT	Area	% Area
1	10.380	152698	0.43
2	12.147	35665907	99.57

(*S*)-**5d**

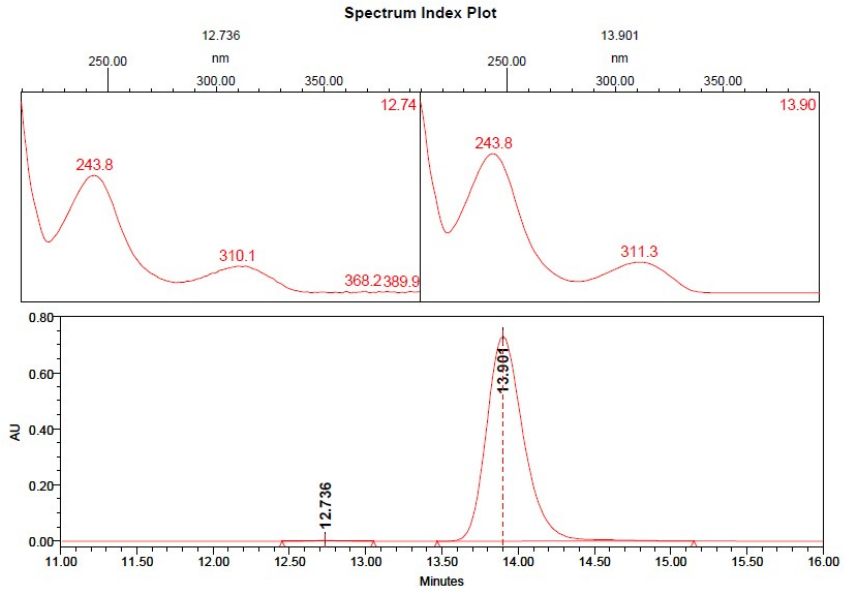
N-(*p*-methoxyphenyl)-1-phenylethylamine (5e)



Peak Results

	RT	Area	% Area
1	12.963	4903461	50.09
2	14.168	4885891	49.91

rac-**5e**

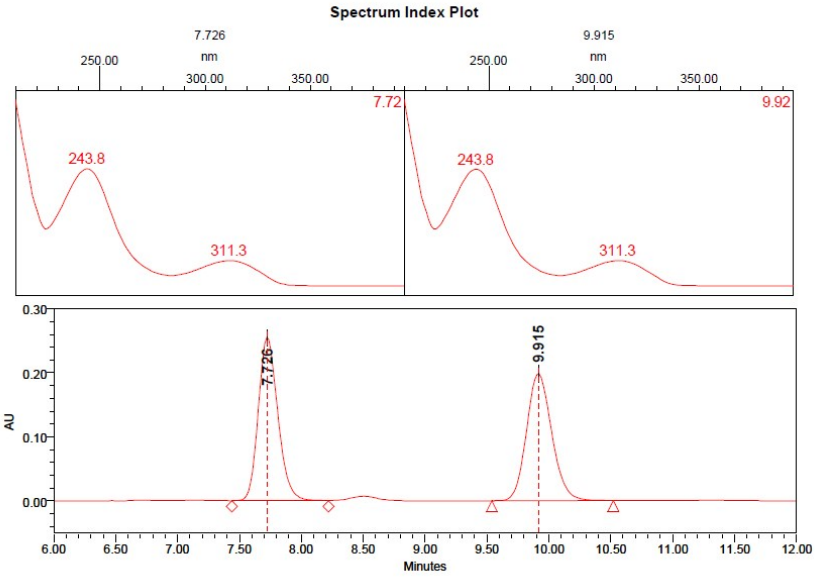


Peak Results

	RT	Area	% Area
1	12.736	31874	0.26
2	13.901	12287040	99.74

(*S*)-**5e**

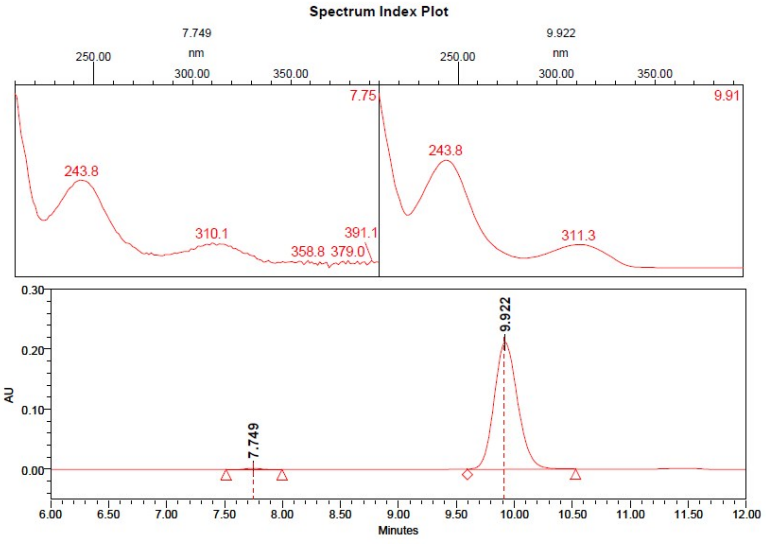
N-(*p*-methoxyphenyl)-1-(*o*-methylphenyl)ethylamine (5h)



Peak Results

	RT	Area	% Area
1	7.726	2808424	50.06
2	9.915	2801894	49.94

rac-**5h**

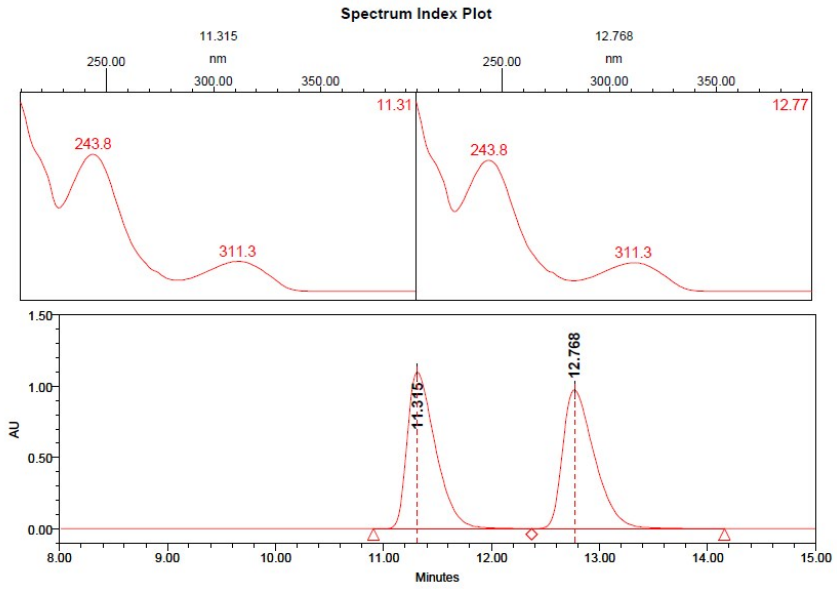


Peak Results

	RT	Area	% Area
1	7.749	18322	0.61
2	9.922	2981671	99.39

(*S*)-**5h**

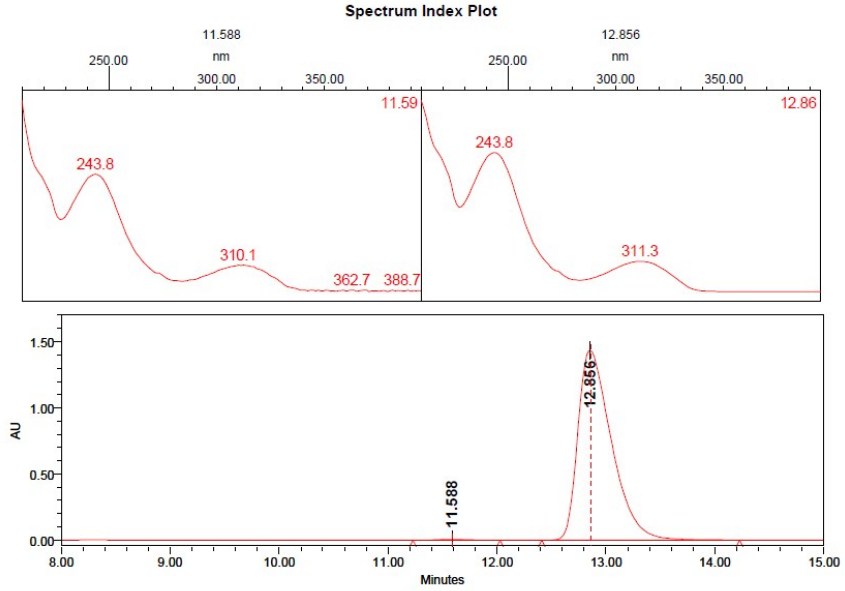
N-(*p*-Methoxyphenyl)-1-(*p*-methylphenyl)ethylamine (5i)



Peak Results

	RT	Area	% Area
1	11.315	19942722	49.98
2	12.768	19959419	50.02

rac-**5i**

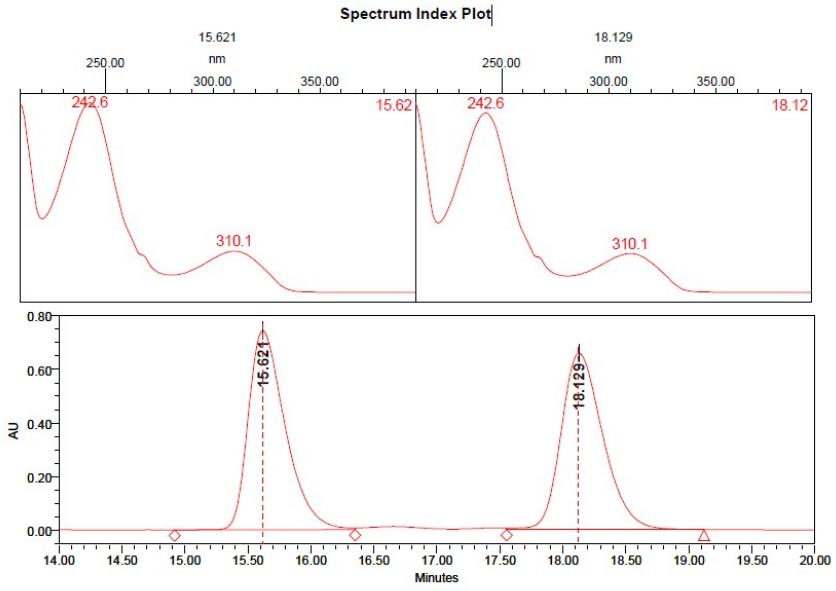


Peak Results

	RT	Area	% Area
1	11.588	104534	0.34
2	12.856	30632429	99.66

(*S*)-**5i**

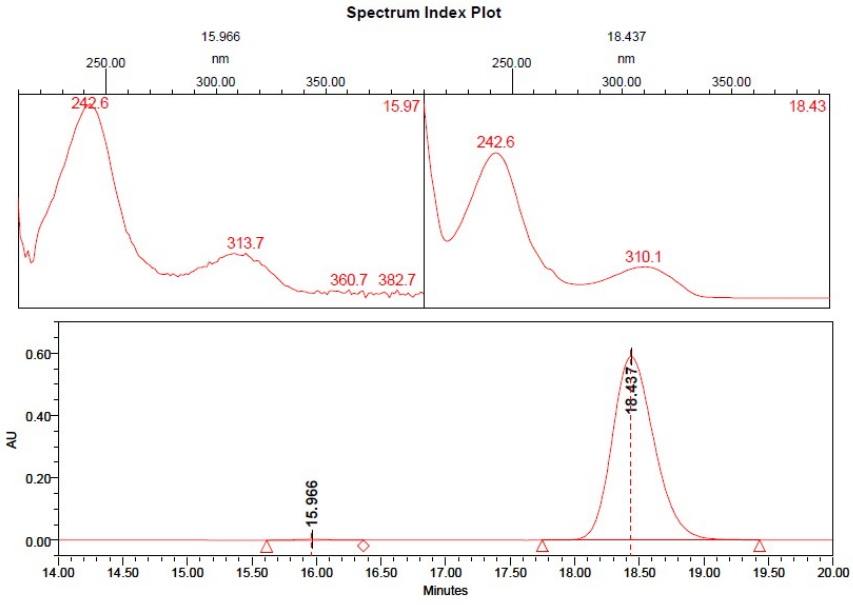
N-(*p*-methoxyphenyl)-1-(*o*-fluorophenyl)ethylamine (5j)



Peak Results

	RT	Area	% Area
1	15.621	15122040	49.93
2	18.129	15166285	50.07

rac-**5j**

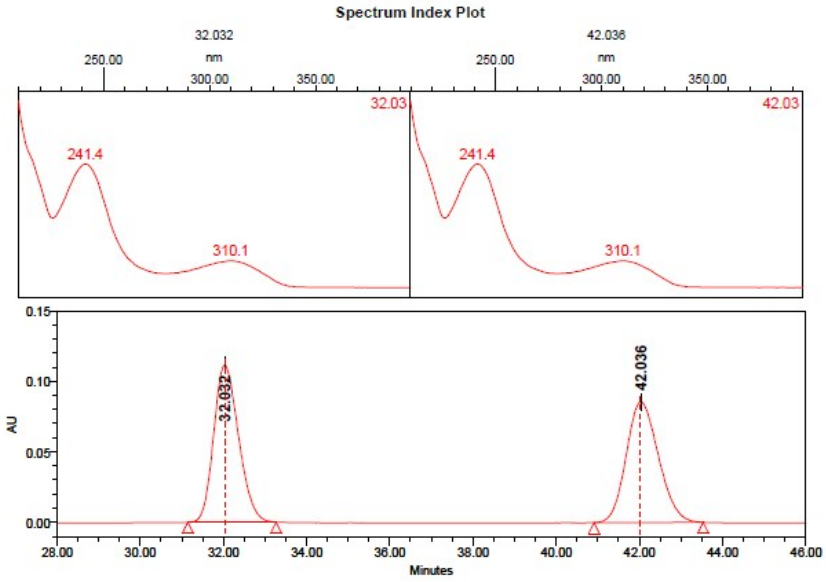


Peak Results

	RT	Area	% Area
1	15.966	52564	0.39
2	18.437	13256683	99.61

(*S*)-**5j**

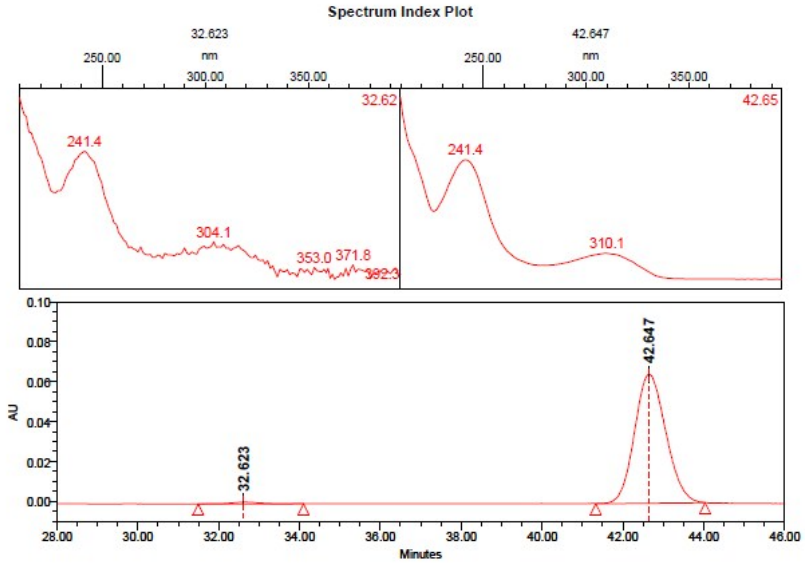
***N*-(*p*-Methoxyphenyl)-1-(*p*-trifluoromethylphenyl)ethylamine (5k)**



Peak Results

	RT	Area	% Area
1	32.032	4643566	50.12
2	42.036	4620627	49.88

rac-**5k**

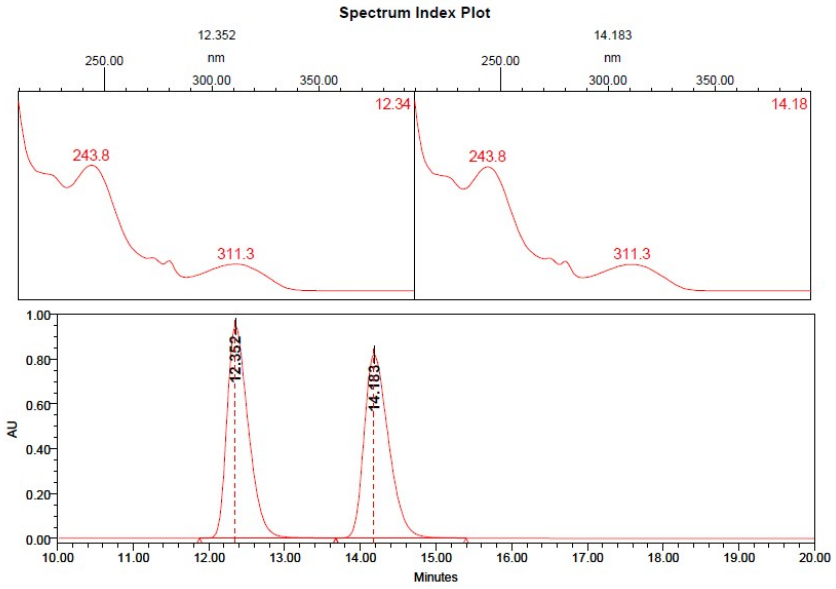


Peak Results

	RT	Area	% Area
1	32.623	40501	1.15
2	42.647	3470161	98.85

(*S*)-**5k**

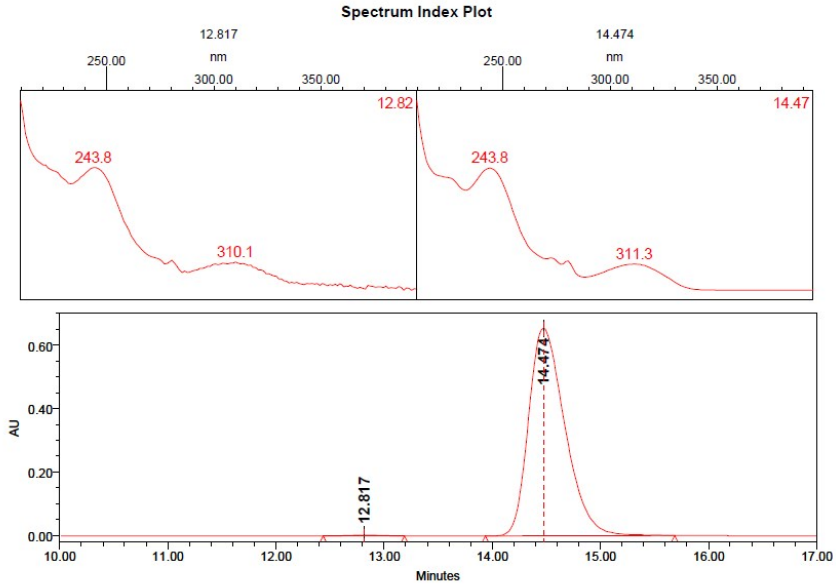
N-(*p*-methoxyphenyl)-1-(*m*-methoxyphenyl)ethylamine (5l)



Peak Results

	RT	Area	% Area
1	12.352	18632640	50.30
2	14.183	18410312	49.70

rac-**5l**

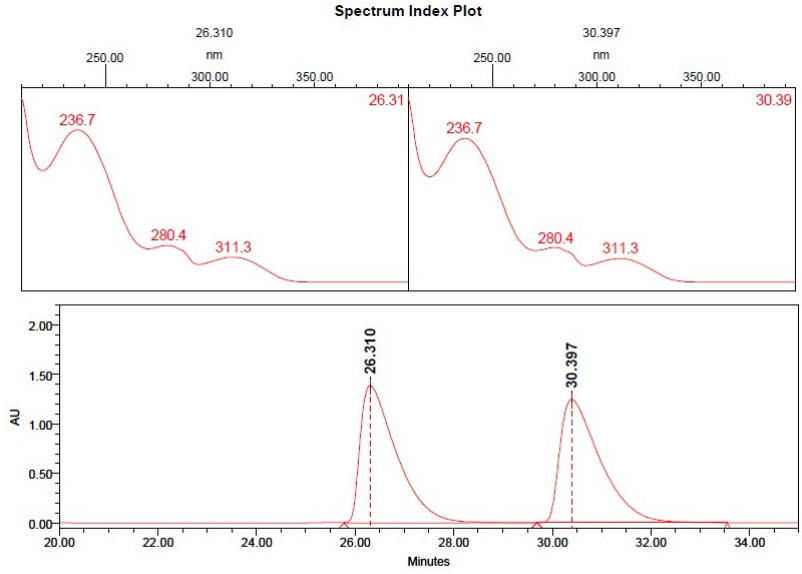


Peak Results

	RT	Area	% Area
1	12.817	44957	0.29
2	14.474	15261539	99.71

(*S*)-**5l**

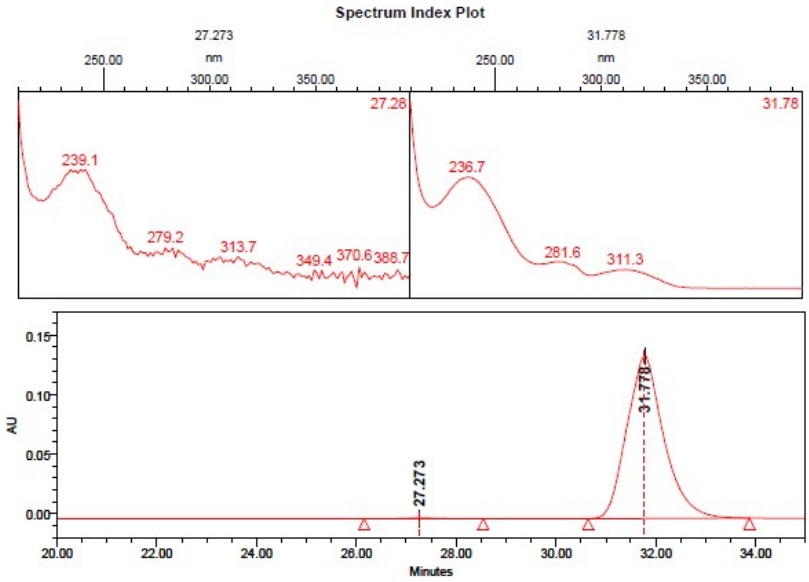
N-(*p*-methoxyphenyl)-1-(*m*,*p*-dimethoxyphenyl)ethylamine (5m)



Peak Results

	RT	Area	% Area
1	26.310	70941829	50.09
2	30.397	70682490	49.91

rac-**5m**

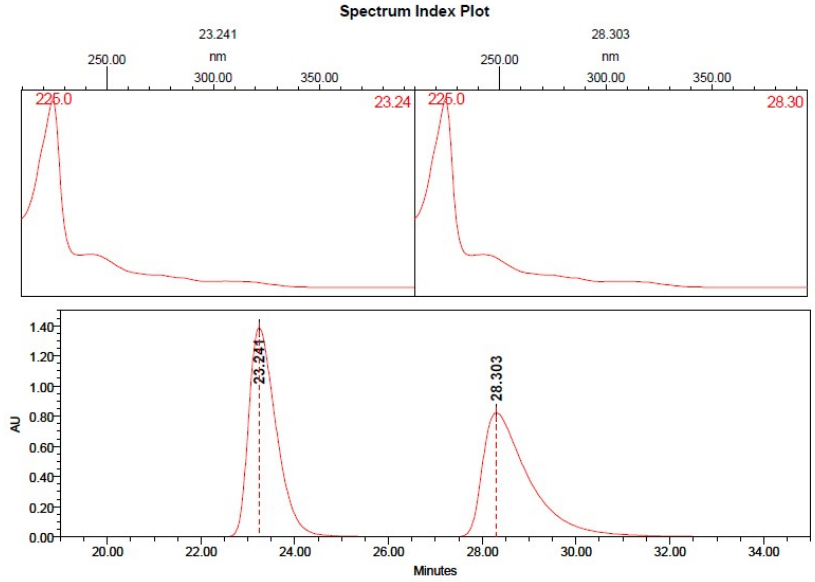


Peak Results

	RT	Area	% Area
1	27.273	29028	0.41
2	31.778	7033712	99.59

(*S*)-**5m**

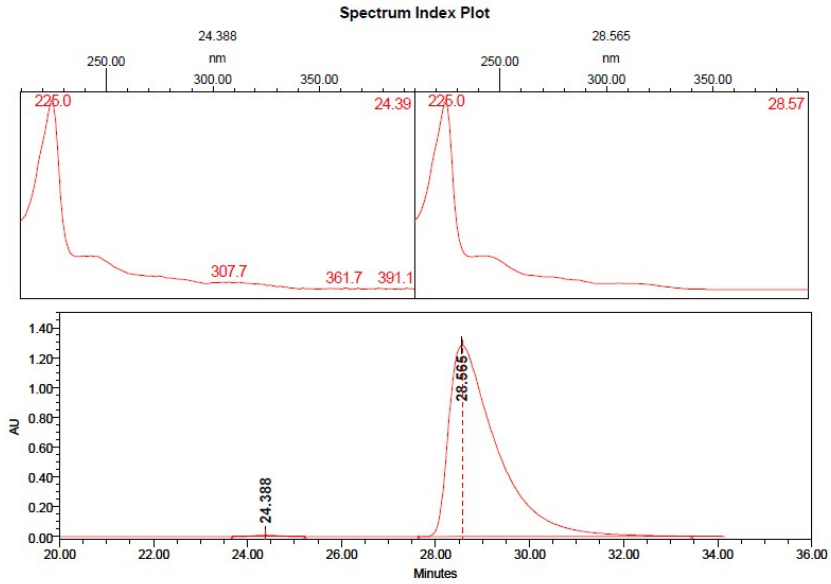
N-(*p*-methoxyphenyl)-2-naphthylethylamine (5n)



Peak Results

	RT	Area	% Area
1	23.241	56344071	50.15
2	28.303	56010524	49.85

rac-**5n**

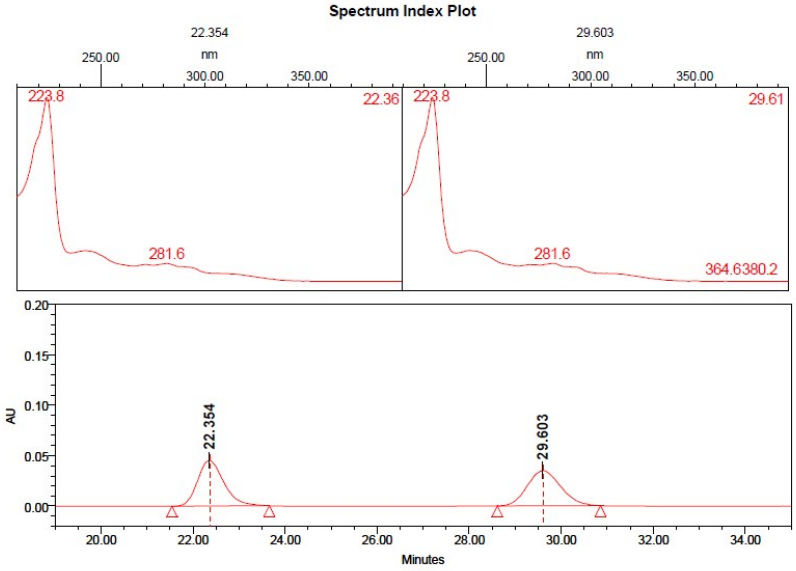


Peak Results

	RT	Area	% Area
1	24.388	378406	0.42
2	28.565	90298100	99.58

(*S*)-**5n**

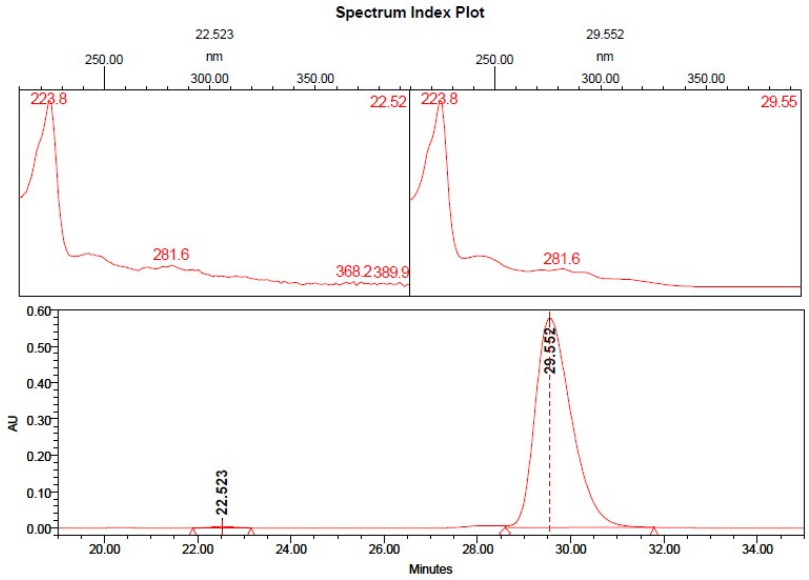
N-(*p*-methoxyphenyl)-1-naphthylethylamine (5o)



Peak Results

	RT	Area	% Area
1	22.354	1796249	50.51
2	29.603	1760014	49.49

rac-**5o**

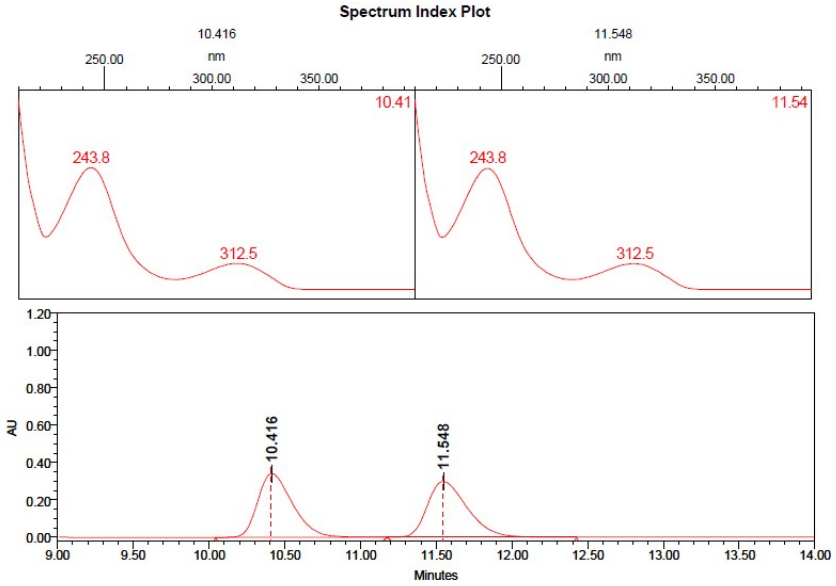


Peak Results

	RT	Area	% Area
1	22.523	129277	0.41
2	29.552	31190589	99.59

(*S*)-**5o**

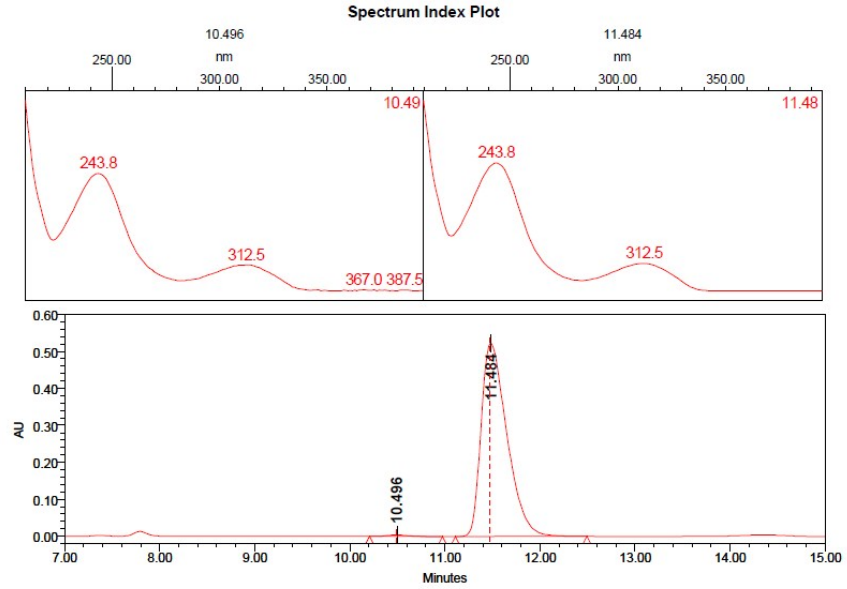
(S)-N-phenyl-1-phenylpropylamine (5p)



Peak Results

	RT	Area	% Area
1	10.416	5452003	49.99
2	11.548	5455051	50.01

rac-**5p**

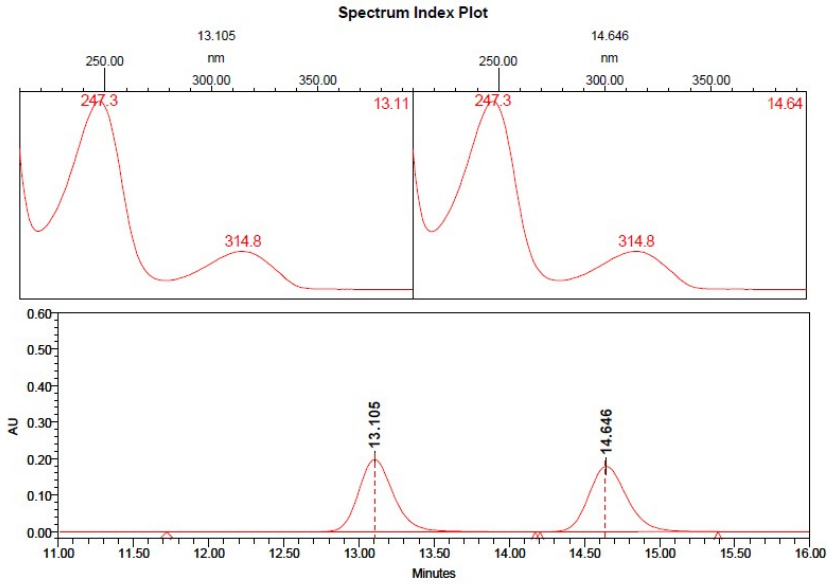


Peak Results

	RT	Area	% Area
1	10.496	54436	0.55
2	11.484	9846739	99.45

(*S*)-**5p**

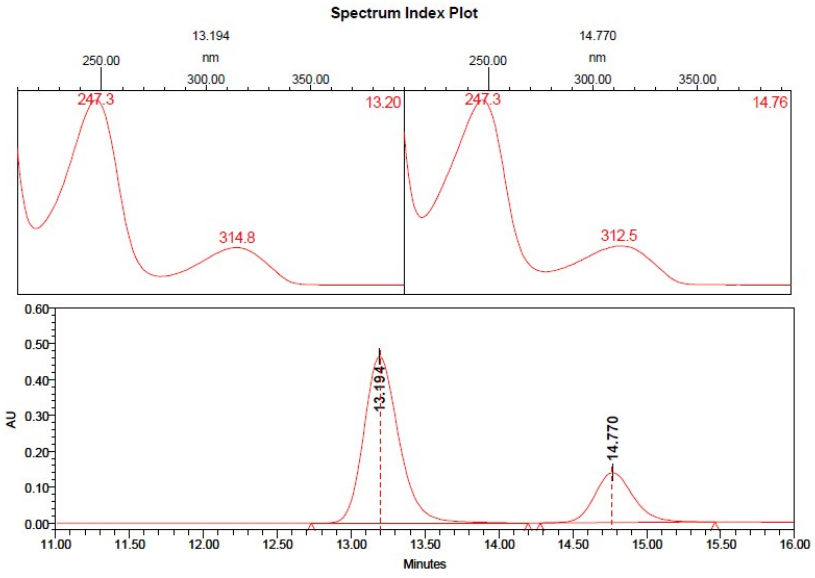
N-(*p*-methoxyphenyl)-1-(isopropyl)ethylamine (5s)



Peak Results

	RT	Area	% Area
1	13.105	3211469	50.35
2	14.646	3166939	49.65

rac-**5s**



Peak Results

	RT	Area	% Area
1	13.194	7627406	75.30
2	14.770	2502110	24.70

(*S*)-**5s** (51 % ee)